CHROMIUM PLATING

WITH SPECIAL REFERENCE TO ITS USE IN THE
AUTOMOBILE INDUSTRY

BY

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WITH INTRODUCTORY CHAPTER
ELECTROPLATING PRACTICE AND THE PROPERTIES
OF CHROMIUM AND NICKEL COATINGS
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TRANSLATOR'S PREFACE

The material contained in the following pages comprises an amplified translation of a report issued by the Staatliches Materialprüfungsamt in 1934, together with an introductory chapter on Electroplating Practice and the Properties of Chromium and Nickel Coatings. The scope of the modifications introduced into the English edition is outlined below.

Additions have been made to the bibliographical references and annotations given in the original, in order to provide a fuller survey of English, American and Continental work on the electro-deposition of chromium and nickel and the properties of metal coatings, and to include publications appearing subsequent to the date of issue of the German report. The additional material is referenced to the text, to indicate the location of further discussion of the respective aspects of the subject dealt with by the authors. In this connection slight modifications in wording have been introduced in certain portions of the text.

In view of the adequate summary of earlier work given in a number of the papers published subsequent to 1920, the bibliography prior to that date has been compiled on a strictly selective basis. An endeavour has been made to include all publications of major importance from 1920 to June, 1935 : those containing a comprehensive review of the literature or specially important experimental work have been indicated by an asterisk. Textbook literature is also specifically designated.

Patent literature, *per se*, has not been included in the bibliography, but a number of the papers listed deal more or less fully with the patent claims made in connection with chromium- and nickel-plating, e.g. 179, 199, 221, 241, 349, 451, 483. Attention is also directed to the Annual Reports of Applied Chemistry (issued by the Society of Chemical Industry) which contain reference to outstanding patent, as well as technical, literature.

After careful consideration of alternative modes of presentation, it was decided to adhere to the original, essentially comparative, form of the report, which consists of introductory chapters covering a discussion of the properties and testing of metal coatings, followed by comparative studies of the respective types of coating on the basis of their behaviour under individual forms of test. Minor modifications have been made

in the arrangement of the text, and some condensation has also been introduced, particularly in the sections relating to corrosion tests.

The translator is indebted to the authors for collaboration in the preparation of the translation, and wishes to make grateful acknowledgment of the stimulating interest and co-operation of Mr. W. R. Barclay, O.B.E., Mr. L. W. Johnson, M.C., M.Met., Mr. A. W. Hothersall, M.Sc., and Mr. W. T. Griffiths, M.Sc., F.I.C., F.Inst.P.

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CONTENTS

PART I

PART II

PART I

ELECTROPLATING PRACTICE AND THE PROPERTIES OF CHROMIUM AND NICKEL COATINGS

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CHROMIUM PLATING

CHAPTER I

INTRODUCTION

The industrial application of chromium plating, which commenced about ten years ago, has contributed largely to the increased interest shown in many countries during recent years in electrodeposited coatings for the protection and decoration of metals which normally tarnish or corrode. The introduction of chromium plating practically coincided with the rapid development of the motor-car industry, which in itself led to a considerable expansion of the market for plated finishes. These developments stimulated a closer investigation into the properties of electrodeposits, with a view to placing the control of the electroplating process on a scientific instead of an empirical basis. Considerable progress in this direction has been made during the past decade and a valuable store of scientific knowledge of electrodeposition has been accumulated. Much of the information, however, is widely scattered and its implications are not generally appreciated. This book fulfils a useful purpose in providing a correlation between the results of research and of practice. The original German edition made a valuable contribution to the knowledge of the properties of typical coatings as produced commercially, but its scope was somewhat restricted by virtue of the nature of the investigation, and the authors have throughout adopted the views generally held on the Continent, without any extensive reference to more recent researches carried out in Great Britain and the United States.

In preparing the English edition, the translator has widened the scope of the book and has corrected its balance by the inclusion of notes referring to electroplating practice and to work, especially of British and American origin, which was not mentioned by the authors. The references have been collected in the form of a bibliography (pp. 224–252) and collated with the text, thus providing a more complete picture of the various problems discussed (see Preface). This introductory chapter has also been added with the object of summarising the more important findings of the book and of relating them to the *process* of

electroplating. Within the limited space available, a full treatment of the subject is obviously impossible : the following condensed summary, however, with the aid of the bibliography, provides a comprehensive survey of the present position of the technique of nickel- and chromium-plating for decorative and protective purposes.

SCOPE OF THE BOOK

The book consists essentially of a description and discussion of results of an extensive examination of typical plated parts of German motor-cars. Fifty-nine representative components, made of steel, brass, bronze, zinc-base die castings and aluminium castings, were obtained from ten German plating firms ; three parts of a French and three of an American car were also examined. Five components only were finished with nickel, the remainder being chromium plated.

Information on the type of coatings applied and their individual thicknesses was obtained from the various participating firms, by means of a questionnaire, the results of which are embodied in Table I. The plated components, together with specially prepared samples of the various materials in sheet form, also plated under commercial con-ditions, were examined for thickness of coating, adhesion and capacity for deformation, hardness and wear resistance, resistance to variations of temperature, porosity, and behaviour in outdoor exposure, salt spray and immersion in sea-water.

Published methods of testing the characteristics of electrodeposited coatings were critically examined. Where no reliable method was available, attempts were made to devise one ; much useful information is given in this connection. New tests for determining the porosity of coatings on zinc-base and aluminium castings were evolved, and methods of testing the resistance of the coatings to wear and to temperature variation were devised.

It should be noted that the thicknesses of the coatings given in Table I, and referred to throughout the book, are those estimated by the plating firms and are not the results of measurements made by the authors. It would appear that the thickness of the undercoatings as measured by the examination of cross-sections under the microscope, corresponded in general with those given in Table I, but discrepancies are apparent in the thickness of certain of the chromium coatings (see, for example, Figs. 7 and 12). These discrepancies do not, however, appear to have influenced the general conclusions drawn from the tests.

The results of major interest are those dealing with porosity and behaviour in corrosion tests : some comments may also be made, however, on the sections dealing with hardness, wear resistance and adhesion.

Hardness and Wear Resistance

In coatings applied for decoration and/or protection from corrosion, hardness is often necessarily of secondary importance, control of other factors such as porosity or thickness being the primary consideration. Similarly, the choice between different types of coating is usually governed essentially by the requirement of resistance to corrosion. Exceptions to these generalisations do, however, arise and whilst it is well known that electrodeposited chromium coatings are remarkable in combining high resistance to tarnish with exceptional resistance to wear, relatively little information is available on the effect of conditions of deposition or of the properties of the underlying metal on the wear resistance. The authors have attempted to bridge this gap by determining the resistance of the coatings to wear, using an improvised apparatus in which revolving felt discs, dressed with a mixture of chromic oxide and paraffin, were lightly pressed against the specimen. Wear resistance was determined by loss of weight (tested at 5-minute intervals) and time required to grind through the coating. The authors conclude that the variable figures which they obtained are partly associated with variations in the conditions of deposition (which, due to the origin of the specimens, were not known) and partly with the type of basis metal or intermediate coating ; they suggest that with soft basis metals or undercoatings, the chromium is soft and shows poor resistance to wear.

Whilst a critical examination of the results might appear to throw doubt on the validity of these conclusions (since, for example, the time required to grind through the coating was, in many of the tests, less than 5 minutes, and the loss in weight of the chromium-plated specimens averaged only 0·0003 g.), the general behaviour of chromium-plated surfaces under abrasive conditions is probably as depicted. Resistance to wear and abrasion is determined mainly by the capacity of the surface to harden by cold working, by the ductility or toughness of the metal (which determines the ease with which particles can be torn out of the surface) and by its resistance to indentation [244, 251]. The behaviour of the metal varies according to the relative extent to which these different factors operate. When hard sharp particles are ground against the surface under a light pressure, the nature of the wearing action is very different from that produced by the heavy pressure of blunt particles or projections. This is especially true of thin, hard chromium coatings on a relatively soft base, since indentation forces tend to deform the underlying metal as well as the deposit. This has the effect of making the surface uneven, concentrating the wear on the high points and, with a brittle coating such as chromium, of inducing cracking and breaking up of the coating. The practical result is that thin coatings of hard chromium tend to offer less resistance to wear on soft

than on hard metals, particularly with wear under heavy pressure. These considerations are probably of more significance than the possible influence of the hydrogen overvoltage of the basis metal on the properties of the chromium coating, to which the authors attribute the differences found in wear resistance with different undercoatings.

The effect of conditions of deposition on the hardness of electro-deposited chromium, and of copper and nickel undercoatings, is too wide a subject to admit of discussion here, but references to recent investigations of the subject have been included in the bibliography. The hardness of electrodeposited chromium, as ordinarily produced, varies approximately over the range 500–950 (diamond pyramid hardness) according to conditions of deposition, and in general it would appear that the conditions suitable for giving a deposit of maximum brightness also yield maximum hardness. The cause of the high hardness of electrodeposited chromium, compared with that of cast chromium (which is similar in hardness to copper), has not yet been fully elucidated.

Recent investigations have shown that the hardness of electro-deposited nickel is due to the inclusion of oxide or basic matter [455] and is not markedly affected by co-deposited hydrogen, as was previously believed. The popular view that hardness is directly connected with co-deposited hydrogen is given by the authors, but it appears probable that for chromium, as well as nickel, this assumption will be superseded by an explanation in terms of included oxide or basic matter [566].

POROSITY AND CORROSION RESISTANCE OF NICKEL AND CHROMIUM COATINGS

The functions of a chromium coating on components of motor-cars, plumbing fixtures, etc., are to impart a pleasing appearance and to provide protection against tarnish and corrosion, so that the foundation metal may be chosen mainly for its cheapness, ease of fabrication or mechanical properties and, as far as possible, without regard to its corrodibility. Since chromium coatings, as normally produced, are invariably porous and contain minute cracks through which moisture can gain access to the underlying metal [192, 331], it is essential (except with basis metals which are resistant to corrosion) that an undercoating should be provided which is relatively immune from corrosion and free from discontinuities. Furthermore, the plated coatings must be sufficiently adherent to the basis metal and to each other to remain intact for a reasonable period and to withstand normal service wear and tear without flaking or blistering.

As a rough approximation, it may be said that the chromium coating affords protection from tarnish, whilst the undercoating provides pro-

tection against corrosion. In practice, thin chromium facings rarely peel from the undercoating and it is the adhesion of the undercoating to the basis metal which is of primary importance both in the plating and in subsequent use. Thus, freedom from porosity and good adhesion of the undercoating are the factors which primarily determine the behaviour of chromium coatings under many conditions. For various reasons, which are discussed in the book, nickel has been found the most satisfactory undercoating in chromium plating and is the one most widely used.

Porosity of Nickel Deposits. Porosity of an electrodeposited coating is strictly defined as the presence of microscopic channels which extend through the coating to the underlying metal. The term is more generally used to embrace all types of discontinuity which result in exposure of the underlying metal.

Little is known at present, except in a general sense, of the causes of porosity in electrodeposited coatings. Practical experience of nickel deposition has indicated that porosity is increased when solid matter is present in suspension in the solution and that inclusions in the surface of the basis metal give rise to pores in thin deposits. Bagging of anodes and continuous filtration of solutions have been adopted in many plants to remove solid matter which tends continually to be formed in the solution (for example by precipitation of iron compounds) and to restrict the amount of anode slimes in suspension. It has also been found that an intermediate coating of copper, formed in the acid sulphate solution, tends to bridge over imperfections in the surface : this method is sometimes used when plating metals containing numerous surface defects [90, 212]. When applied to a ferrous base, it is of course necessary to deposit a preliminary thin coating of copper, from the cyanide solution, or of nickel [233], followed by copper from the acid sulphate bath ; this copper deposit is sometimes buffed before application of the final nickel coating.

A further cause of porosity may be the presence of cracks due to a highly stressed and very brittle condition of the deposit. With unsuitable conditions of deposition (for example too high pH or current density, too low temperature or nickel content of solution), and also in the presence of certain impurities in the solution (especially those of an organic colloidal nature), nickel deposits tend to be lustrous, hard and brittle. As with chromium deposits, lustrous nickel deposits usually contain cracks and are very brittle. These effects are apt to become more pronounced as the thickness of deposit increases, and are specially liable to occur on projecting areas which receive a higher current density than the remainder of the surface. Furthermore, if the part is subjected to bending or deformation in use, porosity may arise as a result of the formation of cracks in brittle coatings.

In spite, however, of precautions taken to ensure clear solutions, basis metals free from inclusions and sound deposits of good mechanical properties, thin nickel deposits are usually found to be porous and the causes of the porosity are at present not precisely known.

Investigations carried out in America have, however, shown that the porosity of electrodeposited coatings of nickel decreases with increase in thickness of coating [134, 183]. This conclusion was confirmed in the present investigation for coatings produced in the ordinary course of industrial plating. Results of atmospheric tests and porosity tests (see pp. 159, 194, 211) were in good agreement and showed that the protective power of chromium coatings on ferrous components bore a definite relationship to the thickness of the nickel undercoat ; when this exceeded 0·001 inch in thickness (and particularly when it was greater than 0·0015 inch) the coatings were relatively free from pores and afforded good protection against corrosion.

The results agree with those recently obtained from co-operative tests carried out by the American Society for Testing Materials, the American Electroplaters' Society and the National Bureau of Standards [485] (see p. 220). It may be mentioned that it was also found in these tests that the thickness of the chromium coating played a part in determining the behaviour on exposure, especially in an industrial atmosphere. The usual thickness of decorative chromium coatings in America was reported to be 0·00002 inch (0·5 μ) which corresponds almost exactly with the average thickness of the chromium coatings (applied over undercoatings) tested by the authors. The American trials showed that although the porosity of the chromium coatings increased with their thickness (due to cracking), an increase in thickness to 0·0001 inch (2·5 μ) over a nickel coating 0·001 inch (25 μ) in thickness on steel improved the protective value. The suggestion is made that for use under severely corrosive conditions, such as an industrial atmosphere, a thicker chromium coating could with advantage be applied.

Further confirmation of the relationship between thickness, porosity and protective value of nickel deposits is provided by results obtained by Baker, Jacquet and Anderson [191, 398, 478]. The writer's experience is also confirmatory for deposits produced under commercial conditions. Thus, it is now established by independent investigations, carried out in four separate countries, that freedom from porosity and high protective value in nickel deposits are synonymous and can at present be secured commercially only by the deposition of a coating 0·001 inch or more in thickness.

In spite of the well-known inferiority of thin, porous electrodeposits on ferrous materials, it is interesting to note that out of the twenty ferrous components obtained by the authors for examination, only four had coatings greater than 0·001 inch in thickness and that on twelve of

these components the total thickness of plated coating was less than 0·0005 inch. It is not surprising, therefore, that in general the ferrous components showed poor behaviour in the corrosion tests.

Thin porous coatings (less than 0·0002 inch, 5·0 μ, in thickness) were also found on the six zinc-base and the two aluminium castings examined. These components quickly corroded in the tests applied. The authors conclude that these metals, when plated with thin porous coatings, are unsuitable for use involving exposure outdoors and should preferably be used for indoor fittings only. Although methods have been advocated in the literature for obtaining relatively thick, non-porous nickel coatings on zinc [325] and aluminium [230, 324, 369, 415, 421, 480], there appears at present to be some difficulty in practice in securing sufficient adhesion to prevent peeling or blistering of such coatings during plating or finishing, and there is a need for further research in this direction.

When considering the relationship between thickness and porosity of nickel coatings, it should be remembered that very few components are of regular shape, and as nickel-plating solutions do not possess very good throwing power, the average thickness of coating on a component may be appreciably greater than the minimum. As an example, the authors report that on one steel component the maximum thickness of coating was four times the minimum. This emphasises the importance of the use both of plating methods which ensure good throwing power and also of inspection tests which are capable of indicating weak spots rather than average behaviour. Points which have emerged from investigations so far carried out on throwing power (see p. 43) have been (1) the better throwing power of moderately buffered solutions (containing for example boric acid or ammonium salts and a chloride), as compared with that of highly buffered solutions (containing boric acid and a fluoride), (2) the improvement of throwing power resulting from a high concentration of nickel salt and the presence of a chloride [100], (3) the adverse effects of operation at low pH [393, 442] and of the presence of oxidising agents used for the prevention of pitting [100]. The poor throwing power of low pH solutions has been stated to be almost entirely counteracted by the use of a high current density and a high temperature, for example 100 amps. per sq. ft. and 60° C. [393, 442]. Whilst much has been done to clarify the subject and to show the relative importance of the numerous factors which determine the distribution of deposit in practice, there is a gap which has not yet been effectively bridged between laboratory determinations of throwing power and the actual regularity of distribution realised under commercial plating conditions.

In this brief discussion, the protective value of electrodeposited nickel coatings has been shown to be intimately connected with their porosity, which usually bears a definite relationship to their thickness.

Exceptions to this relationship are found with lustrous, brittle deposits : furthermore, thickness is liable to vary over the surface of a component and is not readily tested in inspection.

In general, therefore, the final criterion of the quality of a nickel coating as a protection against corrosion is its porosity, and reliable porosity tests constitute a basis on which inspection tests can be formulated [485, 537].

Tests of Porosity. The chief requirements of a porosity test are that it should give a clear and accurate indication of the number, and if possible of the size, of discontinuities present in the coating, that it should be simple and rapid and that the coating should not be attacked during the test. None of the methods so far proposed entirely meets these requirements and, in consequence, some difference of opinion exists as to the most suitable test for general use.

Two types of test have been chiefly used for nickel coatings on steel— the ferroxyl paper or jelly test [177, 295] (which was used by the authors for steel and, with modification, for copper alloys) and the salt spray test. The results of the salt spray test are frequently reported in terms of the period required for the initial appearance of rust ; this may, however, vary for the same specimen according to the observer's inter-pretation of the degree of rusting which constitutes failure. Strausser, Brenner and Blum [537] have concluded that the salt spray test gives a reliable indication of the quality of the coating only when used as a means of detecting the number of pores. They recommend that it should be continued for 100 hours, at the end of which the specimen should be lightly cleaned, and the number of rust spots counted and their size noted.

The authors used the salt spray test as an accelerated corrosion test rather than as a porosity test, and their results confirm those of the American workers in not revealing any clear relationship (such as emerged from the atmospheric exposure tests) to the thickness or porosity of the nickel undercoating.

The ferroxyl test can be conveniently and rapidly carried out and, if used under carefully standardised conditions, appears to yield results which are sufficiently reliable and comparable for inspection purposes. It is, however, open to the objection that the reagent attacks nickel [537]. The apparent porosity, therefore, increases with the time for which the reagent has been in contact with the specimen ; for the same reason, the results probably vary to some extent according to the method of carrying out the test. If reliable results are to be obtained, standard-isation of the test is obviously necessary. To reduce the attack of the nickel to a minimum, the American workers employed a dilute reagent containing 60 g. sodium chloride and 0·5 g. potassium ferricyanide per litre (the authors used 200 g. sodium chloride and 10 g. potassium ferri-

cyanide per litre), but no comparative tests of the modified reagent are recorded.

A method of porosity testing developed for tinplate [405] would appear to merit consideration as affording a more reliable method of testing nickel coatings on a ferrous base. The method consists of immersing the specimen, from which all traces of greasy matter have been carefully removed, in distilled water at a temperature of 95°–100° C. In the course of a few hours adherent rust spots develop at discontinuities in the coating. The water must be tested initially for acidity with methyl red indicator and additions of acid or alkali made, if required, to give a neutral reaction. The validity of the test for tinplate has been carefully examined and established, and tests have shown that it is equally suitable for nickel coatings on a ferrous base. Since the original publication of the method, improved means of degreasing specimens prior to testing have been developed and these, together with full details of the test as applied to tinplate, have been embodied in a recent publication [565].

No established methods of determining the porosity of nickel and chromium coatings on zinc-base die castings or on aluminium are at present available. The authors developed a method in which the specimen is immersed in an alkaline solution which attacks the basis metal exposed at pores, with evolution of hydrogen. To localise the bubbles of hydrogen, and thus clearly indicate the number and sites of the pores, the solution was made viscous with the addition of sugar (for zinc) or gelatin (for aluminium). The test recalls that proposed by Clarke [391] for detecting the presence of pores in cadmium deposits on steel; in this method the specimen is immersed in 1 per cent. hydrochloric acid solution and bubbles of hydrogen slowly form at the site of any pores in the cadmium coating.

THE ADHESION OF ELECTRODEPOSITED COATINGS

If a plane of weakness exists near to the junction of a deposit and the basis metal, peeling or flaking of the coating may occur however strong the actual bond between the two metals. Three chief types of failure may therefore be found : (1) fracture in the coating, a portion of which remains adherent to the base, (2) clean separation, (3) fracture in the base, a portion of which remains adherent to the coating. Combinations of these types of failure may occur, but it is important to bear in mind that all three are ordinarily covered by the term adhesion, which is generally defined as the resistance to detachment of the coating.

It is also important to differentiate, as the authors have done, between the degree of adhesion and the forces tending to cause peeling. When the adhesion is poor, equally adherent deposits may peel under certain conditions of deposition and not under others ; one important

cause of such behaviour, sometimes erroneously attributed to differences in adhesion, is a difference in the stress in the deposit.

The authors have discussed the forces tending to cause detachment of the coating, under the headings of stress in the deposit, dimensional changes in the basis metal, differences in thermal expansion and stresses produced by external forces which cause deformation. They have drawn an important distinction between adhesion and capacity for deformation and have shown that poor adhesion is not necessarily an indication of low capacity for deformation. Certain of the coatings, for example, showed no signs of flaking or blistering in deformation tests in which a steel ball was pressed into the surface of the plated metal, whereas the same coatings could readily be peeled from the metal. Similarly, a bend test is shown to have little or no significance as an indication of the relative adhesion of different deposits unless the properties and thickness of both deposit and basis metal are identical for the specimens being compared. It can readily be appreciated that a hard and brittle deposit which is poorly adherent may flake on bending if it is thick but not if it is thin, and also that a soft ductile deposit, equally thick and poorly adherent, may show no signs of peeling.

Although the Brinell type of test and the bend test were used by the authors, they were clearly recognised as being an unreliable indication of adhesion and suitable merely for determining the capacity of the coating to withstand the particular type of deformation applied.

The only type of test so far found to give reliable information on adhesion consists in tearing or pulling the coating from the base. For application to thin deposits, this test involves reinforcing the coating to enable a grip to be obtained. This can be done by soldering a strip of metal to the coating, but the local heating may invalidate the result and a more reliable method consists in building up a thick coating by electrodeposition of a metal preferably of a different colour to that of the deposit under examination. The method is not suitable for general use, chiefly because of the time taken to build up the coating, but it is capable of giving reliable results and has proved of value for purposes of investigation [348, 444].

The Relation between Adhesion and Behaviour under Corrosive Attack. Due to the fact that no discriminating adhesion test has been used in conjunction with corrosion tests, no correlation is yet possible between the adhesion of an electrodeposited coating and its behaviour under conditions leading to corrosion. It is significant that the failure of the coatings in the exposure and salt spray tests described by the German authors was accompanied by blistering or flaking in local patches. Early failure by blistering or flaking was especially pronounced on the zinc-base and aluminium components, on which the coatings were shown to be poorly adherent. Blistering of a number of the

nickel- and chromium-plated steel specimens was also recorded in the recent American exposure tests [485].

Corrosion at the site of a discontinuity in a nickel coating will tend to undermine the coating to a certain, initially small, extent. The pressure exerted by the corrosion products will then impose a tearing stress on the junction between deposit and base immediately surrounding the discontinuity (see p. 141). If the coating is sufficiently lacking in adhesion to become detached under the stress, the corrosion will spread to the basis metal so exposed and a blister will be formed. It remains to be determined to what extent differences in degree of adhesion contribute to the rapidity of this process, which will, of course, be influenced also by other factors such as the severity of the conditions of corrosion and the corrodibility of the basis metal.

An example of the effect of adhesion on the tendency to blister in outdoor exposure was obtained at Woolwich [disc. on 444] in an experiment in which two steel plates were coated with electrodeposited nickel to a thickness of 0·0003 inch (7·5 μ) ; one plate was treated to obtain a highly adherent deposit, the other to give a very poorly adherent coating. After exposure outdoors for two months, the plates were covered with rust spots and stains and the poorly adherent coating showed numerous large blisters ; no blistering or flaking was detected on the specimen with the strongly adherent coating.

Further investigation of the relationship between adhesion and behaviour in corrosion is required. With existing knowledge, the possibility of some significant correlation cannot be dismissed, and for good quality coatings, an endeavour should be made to secure maximum possible adhesion, consistent with economic working.

The Production of Adherent Nickel Coatings. Methods of cleaning which had previously been used by many platers in the nickel-plating of steel and brass were found inadequate when chromium plating was introduced and when the speed of the nickel-plating process and the thickness of coating applied were increased. This was partly due to mechanisation of the process, which required less individual attention and which eliminated hand scouring, and partly to the increased stress in the nickel coating due to its greater thickness or to the chromium-plating process. Nickel expands when hydrogen is evolved at its surface by cathodic treatment and contracts when the evolution stops [68]. The vigorous discharge of hydrogen which accompanies chromium deposition is therefore liable to cause blistering or peeling of the nickel if the adhesion is poor. An improvement in the technique of cleaning was thus found necessary in order to avoid an undue proportion of rejects in the plating shop.

The chemical cleanliness of metal surfaces has long been recognised as essential to the production of adherent electrodeposits, but the

difficulty of removing traces of greasy matter and the deleterious influence of adsorbed soaps and other colloids [447] has only recently been made apparent. Many improvements have been made in the technique of metal cleaning (see p. 49), the chief of which has been the substitution of mildly alkaline solutions, containing reagents capable of emulsifying greasy matter and of peptising solid impurities, for the strongly alkaline solutions previously used, which functioned mainly by saponification [318]. Soaps are frequently present in cleaning solutions because of their valuable detergent properties, but some soaps are strongly adsorbed by metal surfaces and cannot readily be removed by rinsing ; such adsorbed films may be an important cause of poor adhesion. The modern tendency is to use cleaning solutions containing soaps of free rinsing properties [520, 531] and to reduce to a minimum the contamination of the cleaning solution by preliminary removal of the majority of greasy matter in a solvent vapour apparatus [507]. The passage of an electric current through the cleaning solution considerably accelerates the cleansing action ; the articles are made cathodic. Thorough rinsing, after cleaning, in clean water free from acidity is of major importance ; if any cleaning solution containing soap or an emulsion of grease remains on the surface after rinsing it is likely to lead to poor adhesion, due to the release of greasy matter by the action of a subsequent acid cleaning solution or of the plating solution. The use of hard water for rinsing may result in the precipitation of a film of calcium soap which is likely to be detrimental, and it is sometimes the practice to soften hard rinsing water, a simple method being the addition of a small amount of sodium carbonate.

Whilst poor adhesion, leading to peeling, is probably largely due to the inefficiency of the methods used for removing grease and dirt, it may also be caused by a brittle condition of the deposit or, more particularly, of the surface of the basis metal. The surface of metals is frequently in a highly distorted condition, particularly after polishing, which produces a very thin surface layer of amorphous structure. This layer is very susceptible to embrittlement during plating, due to the occlusion of hydrogen, and deposits formed on a polished or emeried surface can frequently be readily peeled off, fracture taking place in the brittle surface of the basis metal. Light etching removes the layer specially susceptible to embrittlement [348, 444].

The improvement in adhesion obtainable by the use of etching, has resulted in the adoption in many plants of anodic etching treatments for steel and brass. Steel is usually etched anodically in a fairly concentrated solution of sulphuric acid [199, 290, 381] and if the process is suitably controlled, the attack on the metal is slight and the surface is not markedly roughened. Brass may be etched anodically at low current density in a cyanide solution, or in an acid ammonium citrate

solution : the difficulty of polishing the deposit is not increased with this method, as it is with more drastic etching procedures which markedly roughen the surface.

A very high degree of adhesion is thus obtainable and quantitative tests have shown that the separation of thick nickel deposits from steel or brass, which have been suitably etched prior to plating, involves the application of a stress approximately equal to the breaking load of the deposit or the basis metal, whichever is the weaker [444].

THE VALUE OF SPECIFICATIONS

The two most important properties of an electrodeposited coating of nickel and chromium have been shown to be freedom from porosity and good adhesion. With proper control of the process, coatings of good quality can be obtained in practice on brass and steel, although certain limitations may be imposed by the quality of the basis metal and the shape of the article.

A good-quality coating having a high protective value is, however, indistinguishable to the eye from one of poor quality, and whilst poor plating may sometimes be due to bad design, to faulty basis metal or to the incompetence of the plater, it is more generally attributable to price-cutting, which is encouraged by the absence of specifications.

Specifications provide a guarantee of quality to the purchaser and safeguard the interests of the reliable plater. The need for specifications for electrodeposited coatings has been apparent for some years, both in this country and abroad, and in some countries specifications of various types have been in use for some years. Examples are referred to on pp. 38–43 ; other process or purchasing specifications which are not generally known are probably also in force.

There are many difficulties in evolving specifications for electro-deposited coatings which will be suitable for general acceptance, but a good deal of pioneer work has already been carried out by the Electro-depositors' Technical Society (in collaboration with the British Standards Institution), and by the American Society for Testing Materials (see p. 19).

Finally, it should be realised that the scientific study of electroplating processes has been widely pursued only since the War. Whilst considerable progress has been made in various directions, with the result that public confidence in the quality of electroplated coatings has increased, further improvement is still required and is possible only by continued research and the application of the results of research to practice. Increased knowledge of the properties of electrodeposited coatings, and of methods for their control, will, it is believed, inevitably

result in improvement in the quality of plated products and in the expansion of their field of application.

Such advances are fostered by periodically collecting the results of research and correlating them with commercial practice. This function has been fulfilled in this book by the description of an examination of the properties of nickel and chromium coatings, as produced commercially, by the discussion of the results, and by the provision of a very extensive but selective bibliography. Some years have elapsed since the widely scattered literature of nickel- and chromium-plating was last collected together, and the book thus makes, in diverse ways, an important contribution to the advancement of chromium plating.

PART II

CHROMIUM PLATING

WITH SPECIAL REFERENCE TO ITS USE IN THE AUTOMOBILE INDUSTRY

by

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CHAPTER II

INTRODUCTION

The investigation reported in the following pages was carried out, under Government sanction, at the Staatliches Materialprüfungsamt, Berlin-Dahlem, with the collaboration of the Reichsverband der Automobilindustrie (State Association of the Automobile Industry). It was initiated with the primary object of securing data of a reliable and unbiased character which could be placed at the disposal of industry with a view to raising the general standard of commercial plating.[1] To this end the programme was arranged to comprise (1) the determination of the properties of different types of metal coating and (2) the assessment of their relative service value, as shown by various forms of test.

The Reichsverband der Automobilindustrie obtained for examination a selection of plated automobile components representative of current supply,[2] and in order to provide additional comparative data, with particular reference to the behaviour of coatings deposited under more strictly controlled conditions, a series of specially plated samples was prepared for test by methods identical with those used for the actual automobile parts. The tests were selected to simulate, as closely as

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[1] Attention is directed to a comprehensive series of tests in progress under the joint auspices of the American Electroplaters' Society, the American Society for Testing Materials and the United States Bureau of Standards, designed to determine the relative protective values of different types of electrodeposited coatings on steel and non-ferrous metals [321, 426, 475]. The programme for these tests includes exposure at various locations representative of different types of atmosphere, a study of the service utility of accelerated tests, and an investigation of methods of stripping electrodeposited coatings for the purpose of determining weight and thickness. Two reports have already been published, dealing, respectively, with exposure tests of nickel and chromium coatings on steel [485] and with accelerated tests on a parallel series of coatings [537]. The data so obtained have been used for the compilation of A.S.T.M. Tentative Specifications for Nickel and Chromium Coatings on Steel (see p. 41), and proposals for further tests (on non-ferrous bases) have been published for comment by interested parties [475]. Details of test conditions and certain data contained in the reports are referred to in appropriate sections of the present report, under the designation A.E.S.—A.S.T.M.—N.B.S. See also Symposium on the Outdoor Weathering of Metals and Metallic Coatings [477].

[2] About one hundred samples were submitted, by ten firms, representing the output of some forty plating establishments. See also a parallel study of American automobile parts made by Watts [315].

19

TABLE I—Metallic Coatings on Automobile Components

Basis Metal	Exterior Coating	Component	Serial Number	Mark	Type of Coating	Intermediate Layers, μ — Copper	Intermediate Layers, μ — Nickel	Exterior Coating Thickness, μ — Nickel	Exterior Coating Thickness, μ — Chromium	Fig.	Surface Condition of Plating; Type of Plating	No. of Samples	No. of Firms using Type of Plating; No. of replies
Iron or Steel	Nickel	Ornamental hub cap	1	C7	Copper-nickel	3·0	—	5·0	—	1	Yellow-grey tarnish; semi-matt	1	4
		No samples							Chromium				
	Chromium	Door handle	2	D2	Nickel-Chromium	—	3·0	—	0·3		Slightly dull	2	4
		Front-seat fitting	3	D8		—	5·0		0·4		Bright, lustrous		
		Radiator shell	4	E1		0·4	1·5		0·4		" "		
		Cable protection tube	5	J11		0·2	4·0		0·5		" "		
		Gear handle	6	G11	Copper-Nickel-Chromium	0·2	7·0		0·6	2	" "		
		Radiator shell	7	F1		0·5	8·0		0·7		" "		
		Shock absorber housing	8	G10		0·5	13·0		0·8		" "		
		Lamp bracket	9	G18		0·4	16·0		0·5		" "		
		Bonnet hinge	10	C20		0·6	22·0		0·5	3	" "	10	10
		Lamp bracket	11	F4		0·6	25·0		0·6		" "		
		Bonnet screw	12	N3		0·3	37·0		0·5		" "		
		Lamp cross-bar	13			5·0	8·0		0·5		" "		
		Lamp adjusting arm	14	G10	Brass-Nickel-Chromium	Brass 5·0	Nickel 5·0		0·5	4	" "	1	1
		Ventilating disc	15	K4	Zinc-Brass-Nickel-Chromium	Zinc not determinable	Brass 5·5	Nickel 3·0	0·4		" "	2	2
		Cap	16	K2			3·5	4·5	0·4		" "		
		Wheel disc	17	K6			5·0	5·0	0·4		" "		
		Beading	18	K10	Nickel-Chromium		4·0	8·0	0·4		—		
		No Samples					Copper		Chromium				
		Bumper	19	G6	Nickel-Copper-Nickel-Chromium	Nickel 7·0	Copper 6·0	Nickel 8·0	0·5	5	Bright, lustrous	2	4
		Bumper	20	H1		7·0	35·0	2·0	0·75		" "		
	Nickel	Exterior door handle	21	A4	Nickel			3·0		6	Yellow-grey tarnish; corners	2	No replies
		Lamp fitting	22	C2	Chromium				3·0	7	Slightly dull; showed cracks	2	4
		Running-board rail	23	C4							Bright, lustrous		
		Door handle	24	D1	Nickel-Chromium		Nickel 5·5		0·5		" "		
		Radiator shell	25	G1			2·5		0·5		" "		
		Radiator	26	J5			2·5		0·4		" "		
		Radiator screw cap	27	D4			2·5		0·4		" "		
		Window adjuster	28	E7			3·5		1·0		" "		
		Ornamental hub cap	29	G15			3·5		0·3		" "		
		"Stop" lamp	30	J11			3·5		0·5		" "		
		Cable protection tube	31	M2			3·5		0·6		" "		
		Hub cap	32	M3			4·0		0·5		" "		
		Radiator shell	33					4·0		0·4		" "		

20

Base	Coating	Part	No.	Code	Coating system	Composition		Thickness	Appearance		
Brass	Chromium	Footboard plate	34	F9		Copper	Nickel	0·4			13
		Nut	35	G14		0·5	4·5	0·5			22
		Cap	36	J4		0·5	4·5	0·5			
		Lamp casing	37	C3		0·5	5·0	0·5			
		Bonnet support rail	38	C13		0·5	5·0	0·5			
		Radiator shell	39	N1		0·5	5·0	0·4			
		Hub cap	40	N2		2·5	5·0	0·5			
		Beading	41	K10		0·5	8·0	0·8			2
		Bonnet screw	42	G9		0·8	12·5	0·7			6
		Bonnet casing	43	K8		0·8	14·0	0·8			1
		Lamp casing	44	G3			25·0				
		Bonnet support rail	45	G8							
Bronze	Chromium	Knob	46	G13	Copper-Nickel-Chromium	Copper	Nickel	0·6			3
		Ornamental hub cap	47	G5		0·5	2·5	0·8			5
		Ornamental hub cap	48	F2		0·5	3·5	0·7			
		Radiator shell	49	H		2·5	4·5	0·6		9	
		Windscreen column	50	G17		0·8	4·5	0·6			
		Bearing rod	51	J6		0·6	4·0	0·8			7
		Rail	52	C5	Zinc-Chromium	Zinc 120		0·5 Chromium	Slightly dull	10	No replies
		Handle	53	B2	Chromium	Nickel		1·5	Bright, lustrous	11	
		Steering-column bracket	54	B3		1·5		1·5	,, ,,		1
		Roller bearing	55	B4		2·5		2·5	,, ,,	12	5
		Steering-column bracket	56	B1		3·5		3·5	,, ,,		
		Lock	57								7
		No samples	—								No replies
	Nickel	Exterior door handle	58	A1	Nickel	Nickel 2·0		2·0	Yellow-grey tarnish; semi-matt	13	2
		Interior door handle	59	A3				2·2			1
		No samples	60								
	Chromium	Exterior door handle	60	A2	Nickel-Chromium	Nickel 2·0		0·3 Chromium	Bright, lustrous		1
Zinc-base Die Castings	Chromium	Radiator mascot	61	J1	Copper-Nickel-Chromium	Copper 0·5	Nickel 4·0	0·5	Bright, lustrous; some cracks and pores	14	2
		Radiator screw cap	62	J9		Copper 0·4	Nickel 2·5	0·5			1
		Radiator screw cap	63	E2	Brass-Nickel-Chromium	Brass 0·3	Nickel 1·8	0·5	Bright, lustrous; some cracks and pores		1
		No samples	—		Zinc-Nickel-Chromium	Zinc	Nickel	Chromium			1
		No samples	—		Nickel-Copper-Chromium	Nickel	Copper	Chromium			1
Aluminium Alloy Castings	Chromium	Cover	64	J3	Nickel-Chromium	Nickel 3·0		0·5	Bright, lustrous (porous)		7
		Bracket	65	J8	Nickel-Chromium	4·0		0·4	Semi-matt (porous)	15	2
		No samples	—		Chromium			Chromium			1

21

possible, service conditions to which automobile parts are regularly subject.

Although the use of metal coatings has developed so rapidly, there is a comparative dearth of suitable methods for testing plating and plated parts. An endeavour was therefore made to assess the relative validity of known methods, and to devise additional methods.

The qualities which are of primary importance in metal coatings are :

1. Pleasing appearance.
2. Good adhesion and capacity for deformation.
3. Hardness and resistance to wear.
4. Resistance to deterioration on change of temperature.
5. Resistance to corrosion. (This property is a function of the type of coating, its thickness, regularity and freedom from porosity, and of the difference in potential between the basis metal and the metal of the coating). In addition to the requirements laid down in 1–5 above, the following must, therefore, be posited :

6. Suitable chemical composition.
7. Specified minimum thickness and regularity of distribution.
8. Freedom from porosity.

After due consideration of the requirements enumerated above, the programme was drawn up to incorporate tests of :

1. Composition, thickness and regularity of coating.
2. Surface condition (colour, lustre, surface defects).
3. Adhesion and capacity for deformation.
4. Hardness and resistance to wear.
5. Resistance to changes of temperature.
6. Resistance to corrosion ((a) by determination of porosity, (b) by measurement of potential and (c) by corrosion tests).

The programme embodied suggestions made by the Reichsverband der Automobilindustrie, and was designed to meet the practical requirements of the industry. (The majority of service complaints relate to premature wear and peeling of nickel and chromium coatings, to lack of resistance to atmospheric corrosion, and to inadequate and irregular thickness of coating and the occurrence of mottled plating at joints. In general, fewer defects are reported with regard to nickel and chromium coatings on brass and copper parts than with similar coatings on ferrous metals or zinc- or aluminium-alloy castings.)

Table I gives the list of the parts received. German firms are designated by the letters A to K. Parts of an American car (M) and a French car (N) were also examined. The samples are numbered serially 1–65. The specimens are classified on the basis of the types of coating used on the respective foundation materials, thus providing a convenient summary of current practice.

CHAPTER III

TESTING OF METAL COATINGS

Methods of Identification. Three methods may be used for establishing the identity of metal coatings, viz. grinding and visual examination, metallographic examination, and chemical analysis.

Grinding and Visual Examination. Observation of the colours produced during grinding can be regarded only as a qualitative and preliminary method of determining the nature of metal coatings.

Metallographic Examination. Metallographic examination of polished sections presents certain difficulties of technique :

(*a*) Thin layers of poor adhesive quality are torn off during grinding and polishing operations.

(*b*) Edges are rounded off in polishing and lose their sharpness. (In view of the high magnifications used (500–1500), the slightest dulling effect causes marked interference on the photomicrograph.)

(*c*) On account of the wide differences in hardness between the metal of the surface coating, the intermediate layers and the basis metals, photomicrographs often show strong relief effects. These cause interference colours at the points of transition from one metal to another and the colours so produced may prevent the observation of other intermediate layers.

In the present investigation, the samples were mounted in Wood's metal. The difference in hardness between the chromium plating and the mounting alloy (approximately 9 : 3) was found to cause rounding off of the edges, and the Wood's metal was therefore hardened by additions of zinc and bismuth. As an additional precaution, the specimens were plated with 0·1 mm. of copper prior to mounting.

Qualitative identification by metallographic methods presents no difficulties. Under the microscope, chromium shows a bright white colour, and nickel is darker and has a greyish-yellow tinge, while copper and brass show, respectively, the well-known red and yellow tones, and zinc is characterised by a dirty white colour. Coatings less than 0·2 *μ* thick may give some trouble, but coatings so thin are rare and were found only on a few (ferrous) specimens which had been copper-nickel-chromium-plated. In very thin coatings it is also difficult to differentiate between intermediate layers of copper and of brass. In

23

this connection etching with dilute sodium sulphide solution is useful : copper gives a deep black coloration, whereas brass is scarcely attacked.

Chemical Methods.   Mechanical separation of the coating from the basis metal is rarely possible, and separation by dissolving away the basis metal is practicable only in a limited number of cases [see 237]. Analysis of the composite sample as a single unit establishes the identity of the coating metals only if these do not occur in the basis material, e.g. in the case of nickel- or chromium coatings on brass or steel.   In the case of a brass base it is impossible to determine by this means whether copper has been deposited prior to the nickel and chromium, and with a ferrous base also the result may be of doubtful validity, since with copper plating $0 \cdot 2 \, \mu$ thick the weight of copper on a small sample is of an order which might be present in any commercial steel.[1]   Similar difficulties occur in the determination of copper plating on zinc- and aluminium-base castings.

Analysis of the composite mass as a whole also precludes any possibility of determining whether the coating metal has been applied in the form of a single alloy layer or as a series of pure metals.   In this respect metallographic examination is preferable to chemical methods.

The identity of the outer coating, i.e. nickel or chromium, is easily established by even an untrained eye.   Chromium, when polished to a high lustre, is of a light grey-blue colour, while nickel has a pronouncedly yellow tinge.   (The colour of both the nickel and chromium may be affected to a slight degree by the nature of the underlay and the character of the basis metal :   see p. 48.)   In doubtful cases a simple spot test with dilute hydrochloric or nitric acid may be employed. Dilute hydrochloric acid dissolves chromium, with strong evolution of gas :   nickel is barely attacked by a cold solution.   In dilute nitric acid the behaviour of the two types of coating is reversed :   chromium remains unattacked, while nickel goes into solution, with vigorous evolution of gas, and a green coloration is produced [see also 439]. An outer coating identified as chromium may therefore easily be dissolved away by means of hydrochloric acid (1 : 1), while the metals generally used as underlays, viz. nickel, copper, brass, remain practically unaffected.[2]

The fractional solution of underlays of copper, brass and zinc is a somewhat more difficult matter, and the numerous combinations of metals used in the plating industry still present the chemist with certain unsolved problems.   There is also an urgent need for a simple

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[1] Deiss [434] discusses the limitations of analytical methods and proposes an improved process (for use on copper-nickel-plated steel) which eliminates sources of error introduced by penetration of the coating metal into the base.
[2] For full discussion of methods for stripping chromium, nickel and other metal coatings, see 275, 298, 401, 403, 425, 458.   The matter is also under investigation by the American joint committee (see p. 19).

microchemical method for the determination of impurities emanating from the anode or the metal salts, and for a process of estimation of the gas content of metal coatings, especially hydrogen and oxygen. (In the latter connection see papers dealing with the influence of hydrogen content on hardness, pp. 78 and 53.)

Methods for Determination of Thickness and Regularity of Coating. Thickness of metal coatings is estimated by weighing the sample before and after the electrodeposition treatment, or by calculations based on conditions of deposition [516]. The following methods may be used for determination of thickness of coating on finished articles :

Weighing or Measurement of the Deposited Metal Coating. The method of peeling the coating from the base metal is applicable only with heavy deposits showing poor adhesion. In the case of composite coatings embodying intermediate layers, it is as a rule possible to determine only the total thickness of the coating as an integral whole.

As an alternative to peeling off the coating, the foundation metal may be dissolved away, but this method is obviously limited to cases in which a medium exists which will attack the basis metal but not the metals of the coating(s) [237]. If the coating consists of several different metals, it is rarely possible to separate the component layers.

Quantitative Analysis of the Whole Sample. This method is complicated by the difficulties referred to in the preceding section and can be used only when the metal of the coating is not contained in the foundation material. Chemical analysis, moreover, allows only of the determination of the weight of coating per unit of surface, giving no indication of whether it occurs as a single layer or is composite in character, nor of the thickness of the individual layers.

A further disadvantage of this method lies in the fact that it shows only the *average thickness* of the coating over the whole article and offers no possibility of determining the thickness of deposit on sections specially likely to be faulty, e.g. corners or recessed parts. This fact is of importance, since the protective value of a metal coating depends primarily on its evenness and regularity. Extreme variations in thickness, amounting in some cases to several hundreds per cent., are found in deposits made from baths of poor throwing power (see p. 43) ; in such cases some areas may remain practically unplated. Chemical analysis is therefore not entirely satisfactory as a means of determining regularity of coating.

Metallographic Measurement on Cross-Sections [464, 491, 497]. The utility of this method is limited by the fact that only selected portions of the work can be examined, but a compensatory advantage lies in the possibility of minute exploration of precisely such portions of the plating as are especially likely to be faulty, and of quantitative deter-

mination of variation in thickness. (Some difficulties encountered in
the preparation of sections for metallographic examination are discussed
on p. 48.) In the present investigation the thickness of the coatings
is expressed in thousandths of a millimetre (μ). For conversion table
(μ, mm., inch), see Appendix, p. 223.

    Physico-Chemical Methods. Physico-chemical methods, as used for
coatings of zinc and tin, have not yet been developed to any extent for
application to composite coatings. They are based, broadly speaking,
on the determination of rate or heat of solution when the coating is
dissolved in appropriate media [458, 559] ; rate of solution is measured
by the volume of hydrogen evolved.[1]

    [1] " For chromium, strong hydrochloric acid is used : the length of time from
beginning of gassing to the end is of the order of 10–60 sec. for ordinary plates.
The area for the drop test should be marked out with a wax marking pencil to
prevent the acid from spreading " [568]. See also details of chemical or electro-
chemical methods for determination of thickness of coating described by Glazunov
[503 and 556], Petak [527], Deiss [434], Ballay [479], Pontio [26], Macchia [403]
and Meyer [568].

COATINGS ON THE AUTOMOBILE COMPONENTS

Of the hundred automobile components submitted, sixty-five were examined in detail. In the majority of cases the identity of the basis metals was established by metallographic methods, supplemented, where necessary, by chemical analyses. The following materials were found to be in use as *bases* for the respective components : iron and steel, brass, bronze, zinc-base die castings, aluminium alloy castings.

In order to obtain information on the metals in general use as intermediate coatings, a circular questionnaire was addressed to twenty-two firms engaged in chromium-plating, asking (a) whether undercoatings were used, and (b) which metals were used as intermediate coatings on the respective bases. Table I gives a summary of the replies, together with data on the thickness of the individual interlays and the exterior chromium coatings, and particulars of the basis materials. (*N.B.*—It should be noted that throughout the report the " thickness of coating " figures given in the tables are as estimated by the plating firms and not as determined by microscopic examination. In this connection see remark on p. 4.) In the examination of the individual specimens, e.g., for determination of regularity of coating, etc., thickness was measured, in the majority of cases, on straight or slightly curved surfaces. Variations of 10–20 per cent. were found. Especially marked divergence from the reputed thickness was found at edges, protruding sections and recesses. In all cases where an intermediate layer was used, the thickness of the exterior chromium coating was about 0·5 μ, thicker deposits being found only on components on which the chromium was deposited directly on the basis metal (brass or bronze). Where nickel was used as the exterior coating, the outer layer was considerably thicker. The thickness of the various intermediate coatings varies too widely to allow of striking an average figure.

TYPES OF COATING ON THE AUTOMOBILE COMPONENTS

Basis Metal : Iron or Steel.

Iron or steel was used as foundation metal in the case of radiator shells, radiator screw caps, lamps, lamp brackets, cable protection

tubes, bonnet screws, hub caps, bumpers, gear handles. The type of
steel varied according to the purpose for which the component was
required, e.g. soft deep-drawing steel was used for radiator shells
and hub caps, and silico-manganese spring steel for bumpers. The
majority of the remaining ferrous parts were made from various grades
of mild steel.

The following types of coating were found on the ferrous-base
specimens :

NICKEL.

Copper-Nickel. Only one ferrous specimen was found on which
nickel was used as the exterior coating, indicating that in the
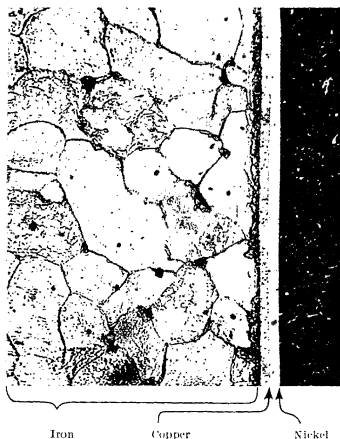
Iron   Copper   Nickel
No. 1 : C 7
Ornamental Hub Cap
(Cu 3 μ, Ni 5 μ)
FIG. 1.

automobile industry chromium has practically superseded nickel as
a surface finish. The thickness of the nickel plating on this sample
(hub cap) varied within wide limits, e.g. on the bore it was 20 μ, and
on straight surfaces only 5 μ. (Fig. 1 shows the coating on a straight
section.)

CHROMIUM.

Direct Chromium (without underlay). Direct chromium plating on a ferrous base appears to be unusual in the case of automobile parts. No examples were found among the components submitted for examination, and of twenty-two chromium-plating establishments from whom enquiries were made, only two reported direct chromium plating as satisfactory.[1]

Nickel-Chromium. On the two components carrying this type of

× 500

Steel   Copper   Nickel   Chromium

No. 6 : G 11
Gear Handle
(Cu 0·2 μ, Ni 7 μ, Cr 0·6 μ)

FIG. 2.
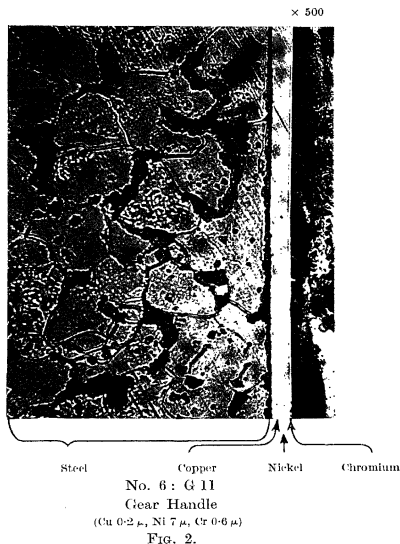
coating the average thickness of the nickel underlay was 4 μ, and of the chromium coating 0·35 μ. This combination is in widespread use : four of the plating plants reported its adoption.

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[1] Mention is made in the literature of a copper-chromium type of coating [117, 221, 336, 346], but no example of this combination was found in the specimens examined, and none of the plating plants reported its use. The recent American tests contain data on coatings in which intermediate layers of cadmium were used [485].

Copper-Nickel-Chromium. On the sample of German origin the copper layer was very thin, varying from 0·2 to 0·5 μ. In contrast to this the French sample, No. 3, had a heavy copper undercoat (5 μ).

The practice of different firms with regard to the thickness of the nickel underlay varies very widely, e.g. the radiator shell E1 carried a nickel layer only 1·5 μ thick, whereas that on the screw F4 was 37 μ. (See examples of varying thickness of nickel in Figs. 2 and 3.)

× 500

Steel   Copper   Nickel   Chromium

No. 12 : F 4
Bonnet Screw
(Cu 0·3 μ, Ni 37 μ, Cr 0·6 μ)

FIG. 3.
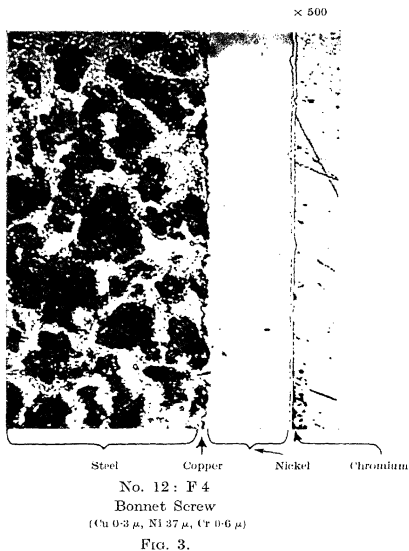
The thickness of chromium varied from 0·4 to 0·8 μ.

The bonding between the respective layers was in all cases perfect.

The copper-nickel-chromium type of coating is very widely used, and was recommended by ten of the plating works.

Brass-Nickel-Chromium. Apparently but little used. One specimen only was submitted for examination (Fig. 4) and only one works reported its introduction.

Zinc-Brass-Nickel-Chromium. Even at a magnification of 1500, it was impossible to determine the thickness of the zinc underlay. The

brass varied from 3·5 to 5·5 μ, the nickel from 3 to 8 μ : the chromium was 0·4 μ thick. Two works reported the use of this type of coating.

Nickel-Copper-Chromium. No samples submitted. One works reported this combination as satisfactory.

Nickel-Copper-Nickel-Chromium. This type of coating is widely

Iron   Brass   Nickel   Chromium
No. 14 : G 10
Lamp Adjusting Arm
(Brass 5 μ, Ni 5 μ, Cr 0·5 μ)
FIG. 4.
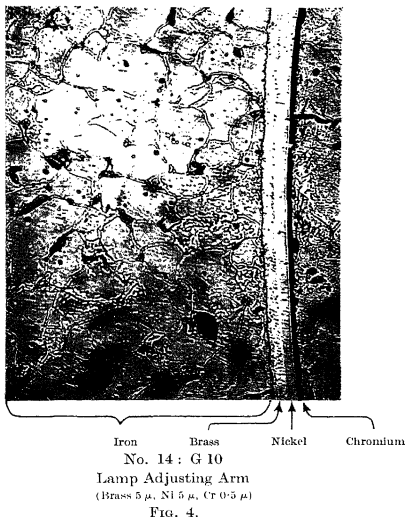
used, e.g. for bumpers and other parts subject to heavy mechanical stress and impact. In view of the character of the service conditions which it is designed to meet, the total thickness of the composite coating is high, e.g. 45–47 μ (see Fig. 5). The 35 μ copper underlay on the American sample M1 is especially noteworthy.

SUMMARY.

Current German practice in the plating of ferrous automobile parts consists, in the majority of cases, in the deposition of a thin coating of copper (about 0·4 μ), followed by a layer of nickel (of widely

varying thickness, viz. 1·5–37 μ), and an outer coating of chromium (about 0·5 μ thick).

The combinations nickel-chromium and nickel-copper-nickel-chromium are also popular. Other types of coating appear to be but little used.

× 200

Iron Nickel Copper Nickel Chromium

No. 19 : G 6

Bumper

(Ni 7 μ, Cu 6 μ, Ni 33 μ, Cr 0·5 μ)

Fig. 5.
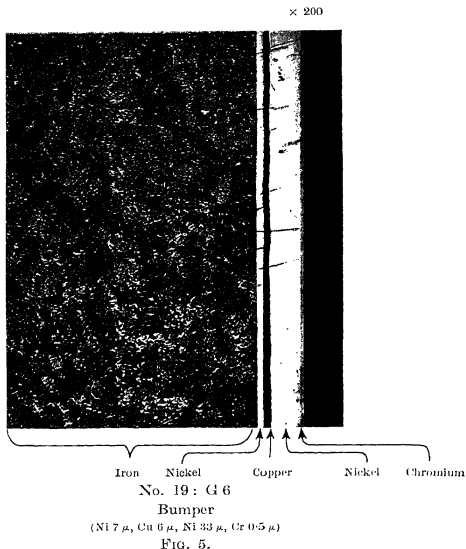
Basis Metal : Brass.

Brass was used as the foundation metal for radiator shells, lamps, hub caps, windscreen columns, bonnet support rails, door handles, badges, bonnet screws. The copper content of typical samples ranged from 55·6 to 63·2 per cent.

The following types of coating were used on brass :

Nickel.

Direct Nickel (without underlay : Fig. 6). On only two of the brass samples was nickel used as the exterior coating, a fact which further confirms the prevailing preference for chromium (*vide supra*).

CHROMIUM.

  Direct Chromium (without underlay). Only one sample of this type was submitted. On straight surfaces the coating was 3 μ thick : at some points along the edges a depth of 6 μ was found. (Fig. 7 is a typical photomicrograph.)

  Replies to the questionnaire indicated that direct chromium plating is somewhat more usual on brass than on a ferrous base : four plating plants reported the practice.

× 500

Brass   Nickel

No. 22 : C 2
Lamp fitting
(Ni 8 μ)
Fig. 6.

  Nickel-Chromium. The majority of the brass parts bore this type of coating, which appears to be very extensively used. The thickness of nickel varied from 2·5 to 25·0 μ, with chromium 0·3 to 1 μ (see Fig. 8).

  Copper-Nickel-Chromium. The thickness of the copper underlay ranged from 0·3 to 0·6 μ, with the sole exception of the radiator shell H, on which the depth was 2·5 μ (Fig. 9). The nickel again varied within wide limits (2·5 to 9·0 μ), while the chromium was 0·5 to 0·8 μ.

  Only two plating plants reported the use of this combination.

Zinc-Chromium. The rail fitting sent in for examination had been hot-dipped, and carried a heavy but uneven coating of zinc (80–160 μ). A distinct diffusion zone had been formed at the brass-zinc contact surfaces (Figs. 10 and 11).

The zinc-chromium combination was not recommended by any of the plating plants circularised.

SUMMARY.

In the chromium plating of brass, current practice favours the deposition of an underlay of nickel. Direct chromium plating is, however, more usual on brass than on a ferrous base. The combinations zinc-nickel-chromium [1] and zinc-chromium are but little used.

Basis Metal : Bronze.

Bronze was used for door handles and locks. The alloy was of the copper 85, tin 5, zinc 7, lead 3 per cent. type.

Only a few samples were submitted, on all of which the chromium had been deposited without an underlay. The thickness of the coating varied from 1·5 to 3·5 μ (Fig. 12).

The replies to the questionnaire indicate a general preference for the nickel-chromium combination, but no parts carrying this type of coating were sent in for examination. (See, however, report on experimental nickel-chromium-plated bronze samples, Chapter XI.)

Basis Metal : Zinc-base Die Castings.

Zinc-base die castings were used for door handles, radiator screws and mascots. Analysis of typical samples showed zinc 92–93 per cent., with aluminium and copper.

The types of coating used on the zinc alloy bases were as under :

NICKEL.

Direct Nickel (without underlay). The average thickness of the nickel was 2·1 μ (see Fig. 13).

CHROMIUM.

Direct Chromium (without underlay). Only one works reported the use of direct chromium plating on a zinc base : no specimens were submitted.

Nickel-Chromium. On the samples sent in for examination the nickel was 2 μ and the chromium 0·3 μ thick. One plant only reported the use of this combination.

---

[1] The A.E.S.—A.S.T.M.—N.B.S. tests [485] showed that the use of zinc under nickel (on steel) reduced the protective value of the nickel and, in most locations, of the nickel-chromium coatings.

× 500

Chromium

No. 23 : C 4
Running-board Rail
(Cr 3 µ)
Fig. 7.

Brass

× 500
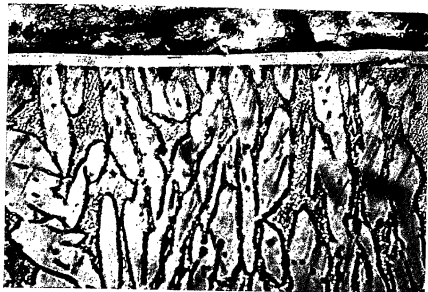
Chromium

Brass Nickel
No. 28 : D 4
Window Adjuster
(Ni 3·5 µ, Cr 1 µ)
Fig. 8.

× 500
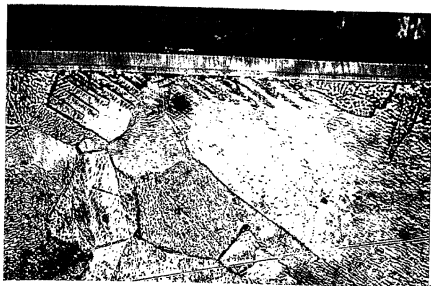
Chromium Nickel

Brass Copper
No. 49 : H
Radiator Shell
(Cu 2·5 µ, Ni 4·5 µ, Cr 0·5 µ)
Fig. 9.

× 500
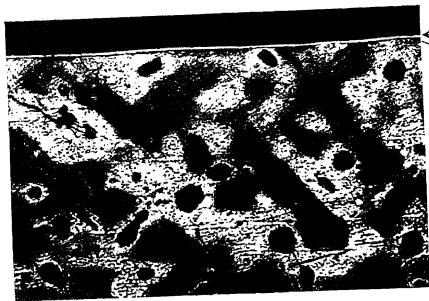
Chromium

Bronze
No. 56 : B 4
Steering-column Bracket
(Cr 2·5 µ)
FIG. 12.

× 1000

Zinc

Brass

No. 52 : C 5
Rail
(Showing brass-zinc diffusion.)
FIG. 11.

× 200

Chromium

Zinc

Brass

No. 52 : C 5
Rail
(Zn 120 µ, Cr 0·5 µ)
FIG. 10.

Copper-Nickel-Chromium. The samples submitted showed copper 0·4–0·5, nickel 2·5–4·0 μ, with chromium 0·55 μ (see Fig. 14). This combination is widely used : five plants reported it as satisfactory.

Brass-Nickel-Chromium. The one sample examined showed brass 0·3, nickel 1·8, chromium 0·5 μ. The combination is widely used and was reported as adopted at four plants.

Zinc-Nickel-Chromium and *Nickel-Copper-Nickel-Chromium.*   Each reported as satisfactory by one plant. No samples submitted.

× 500

Zinc-base die casting   Nickel
No. 59 : A 3
Interior Door Handle
(Ni 2·2 μ)
FIG. 13.
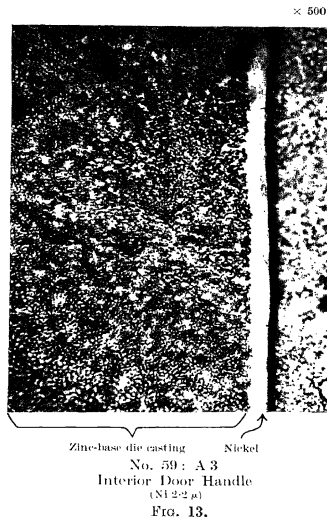
SUMMARY.

In the case of zinc-base die castings, it is usual to deposit a layer of copper or brass, followed by a layer of nickel and an exterior coating of chromium. Other combinations are not used to any considerable extent.

Basis Metal : Aluminium Alloy Castings.

Aluminium alloy castings were found only in bracket supports. A typical specimen, J8, contained copper 10·2, nickel 0·15 per cent., with traces of silicon and zinc. All the samples submitted bore nickel-

chromium coatings, the average thickness of the nickel being 3.5μ and that of the chromium 0.45μ (see Fig. 15).

By all but one of the plating plants interrogated, an undercoating of nickel is regarded as absolutely essential in the chromium plating of aluminium and aluminium alloys.[1]

× 500

Zinc-base die casting   Copper   Nickel   Chromium
No. 62 : J 9
Radiator Screw Cap
(Cu 0·4 μ, Ni 2·5 μ, Cr 0·6 μ)
FIG. 14.
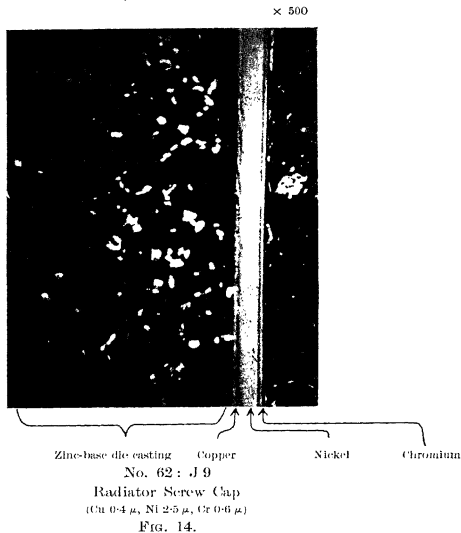
Thickness and Regularity of Metallic Coatings : Specifications

The examination of the representative specimens referred to above indicates that in actual practice the thickness and regularity of metal coatings is frequently much below the standard generally accepted as requisite for securing adequate protection under service conditions (cf. conclusions by Watts [315] and report of examination of products plated to U.S. Federal Specification [538]).

In the interests of the plating and related industries, and of the purchasing public, it is considered highly desirable that the quality

[1] The technique of nickel- and nickel-chromium-plating of aluminium and its alloys is fully dealt with in the literature : see 25, 29, 55, 64, 138, 206, 230, 271, 324, 351, 369, 375, 376, 381, 412, 415, 421, 480, 487, 498, 507.

of metal coatings should be more strictly regulated, by enforcement of existing specification requirements, and by the introduction of new and improved schedules for control of supply of plated products.

Particulars are given below of some specifications already in force for plated goods, and of proposals which have been made for revised schedules :

Carter [493] deals with the practical aspects of inspection and process specifications for nickel- and chromium-plating, and discusses the

× 500
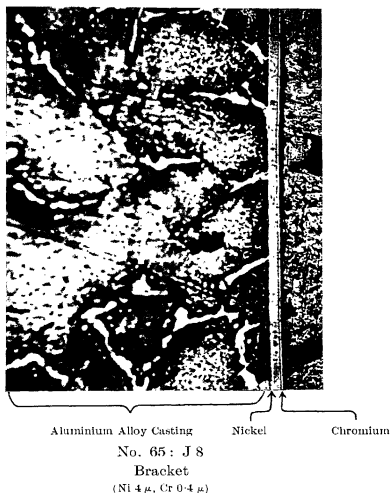
Aluminium Alloy Casting   Nickel   Chromium
No. 65 : J 8
Bracket
(Ni 4 μ, Cr 0·4 μ)
FIG. 15.

specifiable properties of cathodic coatings and the most suitable forms of routine test. The paper includes notes on the following existing specifications for plated products of this type : (1) U.S. Federal Specification W.W.–P.451 (1932) for Nickel Deposits ; (2) a French Railway Specification for Nickel Deposits ; (3) a French Cycle Factory Specification for Nickel-Chromium Deposits ; (4) Specifications published by Messrs. B. J. Round and Son to cover their nickel- and chromium-plated " Epalex " products ; (5) Specifications drawn up by Messrs. Morris Motors, Ltd. for High-Grade Nickel-Chromium Plating for Automobile

Fittings. In view of the close relationship of the Morris specification to the present subject, extracts from it are given below : see also [581].

"In all cases where chromium plate finish is called for, the deposit shall consist of chromium plate with an underlay of nickel or in certain cases, where steel is the basis metal, with a composite undercoat of nickel and copper. In no case will a deposit of chromium directly on the basis metal be accepted."

" THICKNESS OF DEPOSITS

(i) *Nickel Plating on Brass.* The minimum thickness of the nickel deposit after buffing shall be :

$$0 \cdot 001'' \; (= 1 \text{ mil.} = 0 \cdot 025 \text{ mm.})$$

(ii) *Nickel Plating on Zinc-Base and Other Die Cast Alloys.* The minimum thickness of the nickel deposit after buffing shall be :

$$0 \cdot 001'' \; (= 1 \text{ mil.} = 0 \cdot 025 \text{ mm.})$$

(iii) *Nickel Plating on Steel and Iron.*

(a) SHEET. Steel sheet shall be plated with a composite deposit of nickel-copper-nickel. The minimum thickness of each individual component deposit after buffing shall be :

1st deposit nickel .	$0 \cdot 0002''$	($= 0 \cdot 2$ mil. $= 0 \cdot 005$ mm.)
Copper . . .	$0 \cdot 0005''$	($= 0 \cdot 5$ mil. $= 0 \cdot 013$ mm.)
2nd deposit nickel	$0 \cdot 0008''$	($= 0 \cdot 8$ mil. $= 0 \cdot 020$ mm.)

(b) FORGINGS, CASTINGS, SOLID DRAWN PARTS, ROLLED BARS, ETC. Two types of nickel deposit will be permitted. Either the article shall be plated with the composite deposit, nickel-copper-nickel, exactly as laid down above under ' Sheet ', or the nickel deposit shall be plated directly on the steel, in which case the minimum thickness of the nickel deposit shall be :

$$0 \cdot 0015'' \; (= 1 \cdot 5 \text{ mil.} = 0 \cdot 038 \text{ mm.})$$

Chromium Plating over Nickel. The minimum thickness of the chromium deposit shall be :

$$0 \cdot 0001'' \; (0 \cdot 1 \text{ mil.} = 0 \cdot 0025 \text{ mm.}) ''$$

The appendix to the specification contains detailed instructions for carrying out the porosity test on steel, by means of the ferroxyl method as used by Macnaughtan [295].

Bannister [482] gives a critical summary of methods of test suitable for routine inspection, and discusses the advisability of their inclusion in standard specifications for plated products. Sections of the paper deal, respectively, with tests for evaluation of metal coatings on the basis of appearance, thickness, adherence, internal stress, hardness, wear resistance, structure and protective value (the latter as gauged by imitative corrosion tests, porosity, salt spray and corrosion-fatigue tests). See also 384, 428, 540.

For details of existing American Government and commercial specifications for nickel-, chromium- and nickel-chromium-plated products, see 300, 362, 377, 504, 538.

Revision of standard specifications for plated articles is under active consideration by a joint committee of the American Electroplaters' Society, the American Society for Testing Materials, the United States Bureau of Standards, and industrial firms. Recent proposals [548], of which details are given below, are based on experience gained by the extensive series of atmospheric exposure and accelerated laboratory corrosion tests carried out under the ægis of the joint committee: see p. 19.

" Proposed Tentative Specifications for Electrodeposited Coatings of Nickel and Chromium on Steel

1. Scope.

The specifications cover requirements for electroplated coatings on steel articles, including a final coating of nickel or chromium where both appearance and protection against corrosion of the base metal are important. Two types of coating are covered, (1) for general service, (2) for mild service. It is recognised that uses exist for which thicker coatings than those of type (1) will be required.

2. Manufacture.

The steel to be plated shall be substantially free from flaws or defects that will be detrimental to the final finish and shall be subjected to such polishing, cleaning and pickling and plating procedures as are necessary to yield deposits with the desired appearance and quality. The use of copper as an initial or intermediate layer is optional and subject to the requirements specified in Sections 3 and 4. The coatings shall have a bright or dull finish as specified, shall be adherent and free from blisters and substantially free from pits or other surface defects.

3. Thickness of Deposits, Type 1.

(a) Nickel and Copper. For this type of coating on significant surfaces of the finished articles, the minimum thickness of the nickel coating, or of the combined layers of copper and nickel, shall be 0·00075 in., and if copper is used, the minimum thickness of the final nickel layer shall be 0·0004 in.

(b) Chromium. If a chromium finish is specified, the minimum thickness of the copper and nickel layers on significant surfaces shall be as specified in paragraph (a) and the average [1] thickness of the chromium coating shall be not less than 0·00002 in.

___

[1] For many articles the minimum thickness of chromium is more significant, but the average thickness has been specified pending the development of satisfactory methods for measuring the minimum thickness.

4. THICKNESS OF DEPOSITS, Type 2.

(a) *Nickel and Copper.* For this type of coating on significant surfaces of the finished articles, the minimum thickness of the nickel coating, or of the combined layers of copper and nickel, shall be 0·0004 in., and if copper is used, the minimum thickness of the final nickel layer shall be 0·0002 in.

(b) *Chromium.* If a chromium finish is specified, the minimum thickness of the copper and nickel layers on significant surfaces shall be as specified in paragraph (a) and the average [1] thickness of the chromium coating shall be not less than 0·00002 in.

5. THICKNESS MEASUREMENTS.

(a) The minimum thicknesses of the copper and nickel coatings shall be determined by microscopic examination of cross-sections taken perpendicular to significant surfaces.

(b) The average thickness of the chromium coating shall be determined by microscopic examination of cross-sections taken perpendicular to significant surfaces, by stripping methods, or by other methods as agreed upon by the manufacturer and purchaser.

6. CONTINUITY TESTS.

(a) For Type 1 coating the plated articles shall show no appreciable corrosion on significant surfaces at the end of 48-hr. continuous exposure to the salt spray test; and for Type 2 coating at the end of 16-hr. continuous exposure to the salt spray test.

Preparation of Specimen. The specimen shall be cleaned immediately before insertion in the salt spray, so that the surface is free from "water break." This may be accomplished by any efficient method, such as cleaning with a suitable organic solvent followed by light rubbing with a cream of pure magnesium oxide.

Salt Spray Test. The test shall be conducted with a 20 per cent. solution of sodium chloride (sp. gr. 1·15) under conditions that produce a dense fog throughout the container, without the spray being blown directly against the specimens. The latter shall be supported by glass or other insulating material. The temperature in the box shall be maintained by thermostatic control at 95° F. ± 5° F. (35° C. ± 3° C.). The solution formed by condensation of the spray should be drained off and not used again.

(b) Unless otherwise agreed upon by the manufacturer and purchaser, " appreciable corrosion " shall be defined as the presence of more than six rust spots per square foot that are visible to the unaided eye, or of any rust spots larger than $\frac{1}{16}$ in. in diameter.

SUMMARY. The requirements of Sections 3, 4 and 6 are summarised as follows :

Copper plus Nickel	.	.	.	0·00075 in.	0·0004 in.
Final Nickel	.	.	.	0·0004 in.	0·0002 in.
Chromium (if required)	.	.	0·00002 in.	0·00002 in.
Salt Spray, continuous exposure	.	.	48 hr.	16 hr.

[1] See footnote, p. 41.

7. SIGNIFICANT SURFACES.

In general, significant surfaces are those surfaces that are visible and subjected to wear and/or corrosion. The designation of significant surfaces shall be agreed upon by the manufacturer and purchaser, and may be indicated on the drawings.

8. SAMPLING.

Methods of sampling and resampling and the basis of rejection shall be subject to mutual agreement by the manufacturer and purchaser. The number of samples to be selected and the frequency of selection will, in general, depend upon the number of pieces to be plated."

An Appendix to the specification contains particulars of time and conditions required for production of deposits of given thicknesses in copper, nickel and chromium.[1]

The above Tentative Specifications were adopted, in June, 1935, by the Master Electroplaters' Institute of the United States. This body has also issued, for the guidance of its members, provisional specifications covering certain other types of coating on which the Joint Committee is still making exhaustive tests. These schedules include coatings of nickel and chromium on brass, bronze and copper and on zinc and zinc-base die castings [546].

---

[1] The poor throwing power of many plating solutions, especially chromium baths, renders inevitable some variation in thickness of coating. As a result of the closer proximity of the anodes to protruding sections, and due also to current distribution, higher current densities are present at these points than at recessed portions of the cathode.

Problems associated with throwing power, and methods proposed for improving regularity of plating, have been the subject of an extensive literature; see, for example, 75, 76, 100, 167, 259, 280, 283, 285, 304, 305, 311, 313, 319, 333, 340, 350, 389, 393, 409, 414, 420, 436, 437, 442, 449, 458, 462, 468, 483, 507, 544, 567.

SURFACE QUALITY OF METAL COATINGS

Methods of Test

Surface quality of metal coatings is rated according to colour, lustre and freedom from defects. Good nickel plate should be of a yellow-white hue and chromium plate a blue-white colour.

Diffused daylight readily shows up the variations in colour, but in order to secure regular and even illumination, it is preferable to work with diffused light from daylight lamps [311]. Caldwell [discussion on 257] describes, with dimensioned drawing, an inspection bench developed to provide artificial lighting for inspecting chromium plating.

Visual examination is, as a rule, adequate as a means of gauging lustre and for the detection of matt areas. In special cases, e.g. lamp reflectors, specific measurements of lustre and reflectivity may be made. The term " lustre " is here understood to indicate degree of reflective power : the property may be tested by the aid of photoelectric cells, which quantitatively measure the amount of light reflected from the sample [184].

Preliminary measurements at the Staatliches Materialprüfungsamt indicated the desirability of making measurements with the graded photometer, in order to obtain some simple lustre values which should be closely related to subjective observation.[1]

Examination for surface defects will consist, firstly, in finding obvious and coarse defects visible to the naked eye. Microscopically small defects scarcely affect the appearance of the coating, but may exercise a very important influence on its practical service behaviour, since they frequently serve as starting-points for corrosion attack. Metal coatings should, therefore, be microscopically examined in order to detect porous areas, fine cracks, matt patches due to " burning," [2] etc.

---

[1] Kenworthy [512] describes apparatus and a method for quantitative measurement of tarnish on highly polished metals, by reflectivity measurements. The method involves the separate determination of the specular and the diffuse components of reflection, and the use of an empirical formula combining the two properties. See also [471] and description by Digby of reflection meter for use in the study of tarnishing of metals [554].

[2] For details of plating conditions yielding " burnt " deposits, see 167, 221, 223, 275, 359.

Surface Condition of the Coatings on the Automobile Parts

Ferrous Samples. The nickel-plated sample (C7) showed slight tarnish coloration, but a moderate amount of polishing sufficed to restore a high lustre.

The remaining specimens of this class had been bright-chromium-plated,[1] over various forms of underlay. Almost all had a high lustre and were of a good blue-white chromium colour, free from mottled patches. The door handle D2 (nickel 3 μ, chromium 0·3 μ) had a leady appearance, and was somewhat lacking in lustre, indicating that matt chromium had been deposited and that the specimen had been insufficiently buffed.

No. 23 : C 4

Cracks and " Burnt " Areas in Chromium Coating (3 μ) deposited without underlay on Brass

Fig. 16.

Brass Samples. The nickel-plated samples D4 and C2 had become slightly tarnished. The directly chromium-plated running-board rail C4 (chromium 3 μ) was slightly dull, the corners were badly cracked and the plating showed indications of " burning " at the cracks (Fig. 16). The zinc-chromium-plated rail C5 had a rather matt appearance. All the remaining specimens were satisfactory as to lustre and colour.

---

[1] " Bright " chromium plating is almost exclusively used on automobile parts : no matt specimens were sent in for examination. (For details of bright-chromium-plating technique, see 167, 221, 223, 420, 576.) It is possible by buffing to produce a high lustre on matt chromium, but the colour always remains somewhat leaden, and it is preferable, from considerations of colour, of the labour involved in polishing and of the attendant risk of removal of the coating, that the chromium should be initially deposited in the bright form.

Bronze Samples.   The colour and lustre of the (direct-chromium) coatings were satisfactory.

Zinc-base Die Castings.   The surface appearance of the coatings on these samples was somewhat unsatisfactory.   The best specimens were the nickel-plated door handles A1 and A3, which were only slightly tarnished, and the nickel-chromium-plated door handle A2.   The remaining specimens of this group, although satisfactory with regard to colour and lustre, showed coarse surface defects, viz., large cracks and pores.   On the radiator mascot J1 (copper 0·5, nickel 4, chromium 0·5 μ) parts of the surface between the wings had not taken the plating, due, in all probability, to unsuitable arrangement of the work or to the lack of auxiliary anodes.   The existence of the surface defects in J1 and
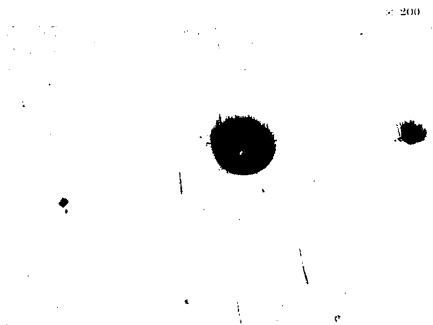
No. 64 : J 3
Porosity in Nickel-Chromium Coating on Aluminium Alloy Casting
FIG. 17.

J9 was confirmed by the porosity test (see p. 112 and Figs. 76 and 77).

Aluminium Alloy Castings.   The nickel-chromium-plated samples J3 and J8 showed numerous pores, which had penetrated deeply into the foundation metal.   The defect in this case was due to the porous condition of the aluminium alloy base (Fig. 17).   The colour and lustre of the chromium plating on J3 were satisfactory, but J8 had a rather leady appearance, and microscopical examination showed flaking and " burning " of the chromium coating (Fig. 18).

SUMMARY.

    Storage for some weeks in the laboratory had produced slight tarnish coloration and considerable dulling of the nickel surfaces, but a

light polishing restored a high lustre, indicating that no actual deterioration had occurred.[1] The chromium-plated samples had preserved their lustre.

× 200
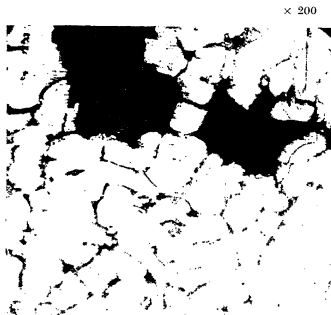
No. 65 : J 8
Flaking of Chromium Coating on Aluminium Alloy Casting
FIG. 18.

The observations made in the present investigation are confirmed by data published by Birett [234], according to which a freshly polished nickel mirror reflects about 65 per cent. and a chromium plate about 55 per cent. of the light projected. After storage for three weeks in damp industrial air Birett found that the nickel retained only 50 per cent. of its reflective power, whereas chromium preserved its original degree of reflectivity.

The reflectivity of metallic coatings naturally varies very widely as a result of variations in methods of production: the lustre of good chromium plating should not be inferior to that of nickel plating. Table II shows values published for nickel, silver and chromium in the region of the visible spectrum.

The type and physical condition of electro-deposited chromium are influenced to an important degree by :

1. The basis metal and its treatment prior to electroplating.
2. The conditions of deposition (composition of bath, temperature, current density, agitation).[2]
3. The thickness of the coating.

[1] Cf. 419.
[2] For general papers dealing with conditions of electrodeposition and resultant variation in the character of the deposited metals, see Bibliography, p. 224.

<div align="center">

TABLE II

REFLECTIVITY OF METAL MIRRORS *

</div>

Electrodeposited Metals.	Wave-length. Å.	Absorption Coefficient, K.	Refractive Index, n.	Reflectivity R : %.
Nickel [1] [2]	5460	2·85	1·81	54·9
	5780	2·97	1·84	56·5
Silver [3]	5460	3·14	0·168	94·0
	5780	3·34	0·172	94·5
Chromium [4] [2] . . .	4500	—	—	72·0
	5000	—	—	69·0
	7500	—	—	62·5

* The values in the table are those given in the original report. For further data on the optical properties of metals see *International Critical Tables*, Vol. V (149), and the individual papers referred to in the footnotes to the table.

It should be observed that the optical constants of very thin films, deposited by electrolytic or other methods, vary materially from the corresponding values for the respective metals in compact form (33).

[1] The value given is based on Lauch [103]. A graphical summary of reflectivity determinations made by various investigators is published by the Bureau of Standards [288].

[2] See also 249.

[3] See 103.

[4] According to Coblentz [238].

1. The Basis Metal and its Preparation for Plating.[1]

Bright chromium can be deposited only on bright surfaces [449]. Metals capable of taking a high polish are therefore best adapted for use as underlays [513, 519] to chromium. Nickel is pre-eminently suitable in this respect and has the further advantage that its white colour has a beneficial effect on the colour of the chromium. According to Cuthbertson [336] chromium deposited on copper is not so bright as that deposited over nickel.[2]

On the majority of the automobile parts examined, the chromium was deposited over a nickel underlay : in no case was the copper-chromium combination used.

Chromium plating on brass is also reported to show, in some cases, a lower lustre than chromium plated over nickel. The only specimen of this type found among the components examined was somewhat lacking in lustre, but in this case the defect was due to burning of the chromium rather than to the nature of the underlying metal. The lustre of the directly chromium-plated bronze samples was entirely satisfactory.

[1] The following papers deal at some length with the influence of the nature of the basis metal on the structure and properties of the electrodeposited coatings : 52, 70, 74, 210, 279, 336, 373, 444, 483, 558, 574. See also papers referred to in " Adhesion " section, p. 51.

[2] Experimental chromium coatings produced at the Staatliches Materialprüfungsamt confirmed Cuthbertson's conclusions. See also p. 168.

No directly chromium-plated steel, zinc or aluminium samples were submitted. The one zinc-chromium-plated brass specimen (C5) was slightly matt. Only matt chromium can be directly deposited on metals so electronegative as aluminium and zinc.

A factor closely related to the influence of the type and physical condition of the basis metal is its chemical treatment. Dirty or incompletely degreased surfaces, or surfaces which after polishing have been exposed for a long time to the atmosphere, often give rise to stained chromium plating.[1]

2. **Conditions of Deposition.** Up to the present, attention has been directed chiefly towards determining the composition, temperature and current density which produce, respectively, bright, matt, burnt, milky or mottled chromium plating.[2] It is known that bright deposits show an amorphous structure, while a matt deposit of greater thickness has many cracks, nodules and crystal nuclei. Knowledge relating to the mechanism of electrolytic crystallisation processes and the relation between electrochemical conditions, the resulting form of the deposited metal and the grouping of the individual crystals cannot yet be regarded as complete (see, however, 43, 52, 71, 95, 117, 169, 279, 373, 374, 396, 431, 465, 483, 508, 553, 555, 558, 562, 574, 579, 580).

The data obtained by X-ray investigation of the form of electro-deposited chromium are also far from conclusive. Both the cubic body-centred form [181] (as found in chromium produced by metallurgical methods) and also the hexagonal form [152] have been observed. K. Sasaki and S. Sekito [366] have also established the existence of a third form, viz. crystals of the alpha-manganese type, and have succeeded in determining certain relationships between current density, temperature and bath composition and the nature of the deposits produced. According to the findings of these authors, only the cubic body-centred form appears to be stable, the others being transformed into the cubic body-centred form after ageing for given periods. (For a review of the findings of these and other authors on this question see 373, 374, 465, 579 and 580. The last-mentioned paper contains the report of experiments made to determine the conditions requisite for the production of the hexagonal form from chromic acid solutions and the structural constants of the deposited metal.)

Since no detailed information was available with reference to the conditions under which the automobile parts had been plated, it was impossible to correlate closely the character of the plating and the conditions of deposition.

---

[1] The literature of cleaning, pickling and related operations is comparatively extensive, see, for example, 91, 199, 230, 231, 246, 283, 290, 315, 318, 322, 348, 416, 420, 421, 422, 432, 433, 450, 473, 485, 507, 520, 531, 581: see also remarks on p. 51.

[2] See p. 45.

E

A detailed discussion of the technique of plating would be beyond the scope of the present report. For information on this aspect of the subject the reader is referred to the very extensive literature on the subject (see Bibliography, p. 224). The main factors involved are very briefly summarised below :

Composition of the Bath. There is an optimum Cr^{iii}/H_2SO_4 ratio and an optimum bath concentration for the production of bright deposits [221, 448, 483. See also p. 45]. The presence of certain foreign ions is requisite [221]. Impurities in the bath cause spotty deposits, and when present in solid form may be deposited at the cathode and give rise to porous and matt patches on the plating [385].

Temperature of the Bath. The temperature of the bath must stand in a given relation to the current density [221]. If too high a temperature is used, certain parts of the work are left unplated or become oxidised : if the temperature is too low, matt patches are formed, or the deposit is burned. (In this connection it is important to note that material of high heat capacity which is put into the bath cold is capable of withdrawing a large amount of heat from the solution.)

Current Density. Attention has already been directed to the relationship between bath temperature and current density (*vide supra*). In plating articles of complex form, throwing power must also be taken into consideration (see p. 43).

Agitation of the Bath. In general, agitation of the bath favours the production of a bright deposit [291]. On the other hand, solid impurities in the bath may thus be projected on to the cathode and give rise to rough and matt deposits [275]. In the case of chromium-plating baths, the evolution of gas accompanying deposition usually causes sufficient movement of the electrolyte, and no artificial agitation is necessary [86].

Thickness of the Deposit. The chromium layers formed in the early stages of deposition are almost always bright, but the production of bright chromium for decorative purposes is practicable only up to a certain thickness, generally about 1 μ (see, however, 485). With thicker deposits cracking sometimes occurs [192, 204, 221, 346].

Surface Defects

The term " surface defects " signifies areas which have escaped plating (or from which the plating has been buffed away), cracks, pores, blisters and nodules [229]. Failure to plate is generally due to lack of throwing power (see p. 43), to inadequate cleaning of the work prior to plating (see p. 49), to the use of an unsuitable form of basis material or to incorrect arrangement of the work in the bath, resulting in the formation, at recesses on the cathode, of gas pockets which inhibit deposition of the coating metal.

The causes of pores and cracks are dealt with in Chapter IX, " Porosity in Metal Coatings."

ADHESION OF METAL COATINGS

The adhesion of metal coatings is a function of two types of force [1] :

1. Atomic or mechanical forces which hold the coating to the base.

2. Forces which tend to detach the coating from the base :
   (a) Forces inherent in the coating.
   (b) Forces inherent in the basis metal.
   (c) Forces due to difference between the coefficients of thermal expansion of the coating metals and the basis metal, which are brought into play by temperature changes.
   (d) Forces produced by cold-working.

1. Adhesive Forces.

Atomic forces are the main factor operating in favour of adhesion; mechanical forces come into play only in exceptional cases, e.g. if the surface of the basis metal is roughened [230]. Maximum adhesion is attained when the adhesive power of the coating is equal to the tensile strength of the coating or the basis metal. Good adhesion is to be anticipated if the crystals of the basis metal continue to grow in the deposited layer, and to this end the crystal systems of the two metals (coating and base) should preferably be closely related, and their lattice dimensions similar [464. See, however, 558, 574].

Formation of a transitional alloy may also favour intimate metallic union between the basis and the coating metals,[2] but the production of such an alloy stratum is in itself no guarantee of good adhesion, since the alloy may be brittle and of low tensile strength. In testing galvanised iron sheet, Bablik [270] found that the adhesive power of the deposit decreased with increasing thickness of the brittle intermediate iron-zinc alloy layer.

Since insufficient cleaning of the basis metal also tends to produce inferior mechanical properties in the transition layer, careful preparation of the basis metal is of paramount importance [271, 348, 360, 444,

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[1] 197, 199, 206, 330, 348, 444, 447, 464, 483, 497, 509, 558, 574.

[2] In this connection see reference to high-frequency oscillatory treatment proposed by Mahoux [297].

449, 497. See also p. 49]. Oxide layers and layers of adsorbed gas are a further cause of faulty adhesion, and it is possible that unsatisfactory results obtained with chromium coatings on aluminium and nickel surfaces previously exposed for some time to the atmosphere may be due to the formation of surface oxide prior to plating, or to the adsorption of gas at the surface of the basis metal [see 6, 199, 449, 513, 519].

2. Detaching Forces.

(a) *Forces Inherent in the Coating.* Certain structural changes occurring in electrodeposited metals may give rise to contraction or expansion of the metal layers, producing stresses which result in detachment of the plating from the basis metal [14, 41, 46, 68, 160, 196, 211, 255, 273, 346, 354, 483.]

In the case of metals which have a tendency to the formation of single crystals, e.g. zinc, an expansion effect is observed [169, 407]. The metallic nuclei grow irregularly, starting from isolated nuclei, and other nuclei gradually force themselves in between the original crystals [71, 82, 169]. In metals having a low capacity for crystallisation, e.g. nickel and chromium, which form closely coherent deposits of amorphous structure, there is, as a rule, a contraction effect [41, 46, 49, 68, 102, 483, 509]. This contraction takes place by a recrystallisation process resulting from intimate contact of the crystals under the influence of atomic and lattice forces. Kohlschütter and Jakober [169] designate the phenomenon the " after effect of crystalline field forces." The secondary crystallisation may consist in a change of size and orientation of the existing irregular crystallites : the extent of the forces exerted is determined by the original condition of the deposited metal layer, i.e. by the degree of dispersion and the arrangement of the metal atoms.

The size, form and orientation of the crystallites as originally deposited are regulated by the conditions of deposition, chiefly by the current density, the bath temperature and the nature of the electrolyte (see p. 49). It has been shown that metals whose deposition is accompanied by the evolution of large amounts of hydrogen show a specially marked tendency to contraction [60].

The stresses produced by contraction may assume very considerable proportions and may exceed the elastic limit of the deposited metal (*vide supra*). In brittle coatings containing a large amount of hydrogen, these stresses may lead to cracking and splitting, whereas in tough and ductile deposits they may be relieved.

Occlusion of hydrogen has a highly deleterious effect on electrodeposited metals, inducing inferior mechanical properties and brittleness (see references to literature on hydrogen content on p. 78).

According to Pfanhauser [175], chromium deposits obtained at a current density of 5 amp./dm.[2] may contain 200–250 times their own volume of hydrogen, and as much as 2000 times their volume when a current density of 20 amp./dm.[2] is used. Hüttig and Brodkorb [126] showed that electrodeposited chromium may contain as much as 0·45 per cent. of hydrogen. Wright [189] found that the hydrogen content of deposits produced under varying conditions ranged from 1000 volumes in a " true matt " deposit to 2000 volumes in a " milky bright " deposit. Hothersall and Hammond [506] found 0·01–0·02 per cent. hydrogen in nickel deposited over a range of conditions. (See also 63 and 107.) Hüttig and Brodkorb [loc. cit.] found that the hydrogen penetrates the lattice of the chromium in an even and regular manner, slightly widening it but leaving it otherwise unchanged. The chromium-hydrogen compound formed is a super-saturated solution of chromium in hydrogen and is not stable ; after a time, decomposition to chromium and hydrogen occurs. In nickel, the absorption of hydrogen may be 13·5 times the volume of the metal : iron may occlude 112 times its own volume [58]. See also summary of hydrogen contents of various electrodeposited metals and discussion of the form in which the gas is occluded [577].

In order to reduce contraction stresses and to obviate brittleness in the coating, metals should be deposited under conditions ensuring minimum evolution of hydrogen [56, 399, 483, 564, 570], viz. high metal ion concentration, adequate agitation of the bath, raised temperature and low current density [577]. Raising of the temperature of the electrolyte, although favouring evolution of hydrogen, appears to lower its solubility in chromium.[1]

Hydrogen may also be evolved from the basis, or underlay metal. Nickel used as an underlay to chromium should, therefore, contain a minimum amount of hydrogen and should be not less than a certain thickness, in order to be capable of absorbing the hydrogen evolved during deposition of the chromium [174, 175, 199, 359, 513].

Stresses may be removed and hydrogen expelled by subsequent heat treatment of the work [316, 566]. According to Hüttig and Brodkorb, expulsion of hydrogen from chromium begins at about 58° C. and is practically complete at 300°–350° C.[2] A method developed by Bosse [175] effects expulsion of gas in vacuo by cathodic sputtering.

(b) *Forces Inherent in the Basis Metal.* Structural changes occurring in the basis metal may also tend to loosen the coating from the foundation. For example, in the case of chromium on brass, a scaly exfoliation of the plating is frequently observed after a period of about two or three months. This effect cannot be explained on the grounds

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[1] See 331.
[2] See also references to heat treatment for expulsion of hydrogen and relief of stress, p. 94.

of conditions of deposition, but is believed to be due to structural changes and stresses occurring in the basis metal [234]. Heat-treatment (at a temperature selected according to the nature of the basis metal) very markedly relieves, or entirely removes such stresses [1] [566]. In view of the likelihood that similar effects would occur in zinc-base die castings, the Die Castings Sub-Committee of the Deutsche Gesellschaft für Metallkunde carried out a series of investigations on zinc-base alloys, in which determinations were made of change in volume as a function of time [139]. The results showed that in aluminium-free zinc-base die casting alloys the changes are very slight, whereas in zinc alloys containing aluminium they are considerable, especially in alloys containing high amounts of impurities. After a lapse of three years, pure aluminium-containing zinc alloys showed a change of 0·085 mm. on a length of 60 mm., as compared with 0·10 mm. in the impure alloys. In tin-base alloys the alteration amounted to only 0·02 mm.[2]

(c) *Effect of Temperature.* Differences between the thermal coefficients of expansion of the basis metals and the metal(s) of the electrodeposit may, when the composite material is heated, give rise to stresses which tend to loosen the coating from the foundation. This effect and the means for its prevention are discussed in greater detail in the chapter dealing with effect of variation in temperature (p. 86).

(d) *Cold-Work.* Stresses which tend to cause peeling of the coating may also be produced by cold-work, the magnitude of the stresses so induced depending on the degree of working and on the mechanical properties of the foundation metal and the metal of the coating. In the case of coatings of metals possessing high capacity for deformation, or metals whose mechanical properties are closely similar to those of the basis metal, the stresses are of a low order only.

Table III gives the average mechanical properties, in the normalised condition, of the metals occurring as foundations or coatings in the automobile parts examined.

In the case of chromium, no data on mechanical properties are available, with the exception of a value for the hardness of electrodeposited metal (see Table III). Due to its high hardness, chromium may be expected to be resistant to wear as represented by sliding friction, but on account of its lack of ductility, it will be sensitive to cold-work effects. Nickel is more ductile than chromium, but is much softer and therefore less resistant to wear.

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[1] See also references to effect of raised temperature of the electrolyte in reducing stress in nickel deposits [211], and [160].

[2] H. Chase [495] discusses the dimensional instability of zinc-base alloys and gives a table showing changes occurring in typical die-casting alloys after varying periods. In certain of the alloys the tendency can be minimised by stabilising annealing treatments, particulars of which are given. See also [424].

TABLE III

AVERAGE MECHANICAL PROPERTIES (IN THE NORMALISED CONDITION) OF METALS USED AS BASES OR COATINGS

Metal or Alloy.	Tensile * Strength Tons per sq. in.	Elongn.* %	Erichsen * Ductility Value (1 mm. sheet)	Brinell * Hardness.	Brinell Hardness Range of Electro-depd. Metal.
			mm.		
Nickel ²	25·5	45	0·48	60	125–550 ¹
Chromium	—	—	—	—	400–950 ¹
Copper ³	13·5–15·5	40	0·465	50	40–300 ¹
Zinc	9·5	20	0·315	30	40–50 ¹
Brass (60% Cu) ³ . .	22·5	20	0·551	65	—
Mild Steel (0·1% C.) .	19–25	25–32	0·433	100	167–350 ⁵
Bronze (Cu 85,³ Sn 5, Zn 7, Pb 3%) . .	9·5–12·5	6–12	—	50–70	—
Zinc Die Casting Alloy ⁴ (Zn 91, Al 5, Cu 4%)	16·5	0·25	—	107	—
Aluminium Casting Alloy (Al 92, Cu 8%) . .	14	2	—	66	—

* The values in the table are as given in the original report. For further data on the mechanical properties and hardness of the respective materials see *International Critical Tables*, Vol. II (149), *National Metals Handbook* (424) and the individual papers referred to in the footnotes to the table.

¹ The values given for the hardness ranges of electrodeposited metals are taken from a recent paper by Macnaughtan and Hothersall, in which a tabular summary is made of the hardness and structural characteristics of metals deposited under varying conditions of bath, temperature, etc. The factors responsible for the modifications in properties are critically discussed [566]. (In connection with the hardness of electrodeposited chromium, see references to the literature, p. 78.)

² The properties of nickel are summarised in a data sheet issued by the Bureau of Standards [288].

³ See also data on the properties of copper and copper alloys summarised in publications of the Copper Development Association [496].

⁴ A comprehensive review of the properties of zinc-base alloys is given by Chase [495].

⁵ See 149.

Adhesion Testing

Due to the absence of any entirely satisfactory method for measuring adhesion, the literature on adhesive properties of electrodeposited metals is comparatively sparse.

Two different types of test have been proposed [132, 348, 444, 458, 510]. The one consists in direct measurement of adhesion by determination of the force required to separate the coating from the basis metal by tearing off or other mechanical method of separation. (This method, although yielding accurate data on adhesive capacity, presents very serious practical difficulties.) The other method consists in observation of the behaviour of the deposited metal during deformation of the basis metal, e.g. during bending. The degree of deformation undergone without flaking or peeling of the coating is taken as the criterion

of adhesive power. Hothersall [348, 444] summarises the salient features of the respective methods and describes qualitative and quantitative tests of adhesion of electrodeposited nickel to brass and to steel.

Although the deformation method of testing indicates capacity for deformation rather than adhesive quality, the behaviour of a metal coating during mechanical working of the basis metal nevertheless gives some indication of adhesive capacity, since when the basis metal is drastically deformed, adherent coatings show only fine cracks and splits, whereas coatings of low adhesive power exhibit coarse cracks and tears which ultimately cause peeling and scaling of the coating. It must be remembered in this connection that the mechanical properties of the basis metal exert a considerable influence on the behaviour of the electrodeposited coating. Basis metals of low ductility will crack when even slightly worked, and although the coating deposited on them may possess intrinsically good adhesive capacity, the cracks from the foundation material may spread into the coating (see p. 58).

TESTS TO DETERMINE THE FORCE REQUIRED TO SEPARATE THE COATING
FROM THE BASE

(a) Tearing off by means of a strip of metal soldered to the coating.

(b) Tearing off by means of a strip of insulating material fixed to the coating.

(c) Tearing the coating from the base by means of direct gripping mechanism [330, 444, 510].

TESTS TO DETERMINE THE DEFORMATION REQUIRED TO PRODUCE
PEELING OR CRACKING OF THE COATING

(d) Tensile straining.

(e) Close-bending.

(f) Reverse-bending (alternate–bending).

(g) Deep-drawing.

(h) Ball-indentation.

Preliminary tests, to determine the relative suitability of the respective methods, were made on two materials, viz. " A," nickel-chromium-coated mild steel strip and " B," nickel-chromium-coated hard brass strip. In each case the nickel underlay was 25 μ and the chromium coating 0·5 μ thick.

(a) *Tearing off by means of a Soldered Metal Strip* [3, 132]. This method is unsuitable for testing chromium plating, due to the fact that chromium cannot be satisfactorily soldered. In the experiments now reported, the strip, with the solder, in every case became detached from the chromium plating. In addition, the method suffers from the fundamental disadvantage that the soldering process affects the properties of the coatings.

(b) *Tearing off by means of a Strip of Insulating Material* [311]. This method obviates the difficulties inherent in (a), but insulating strips, even when satisfactorily adherent, possess a mechanical strength insufficient to effect separation of the coating from the basis metal, and the method is therefore unsuitable for quantitative determination of adhesion.

(c) *Tearing the Coating direct from the Base.* This type of test can be used only for thick coatings. According to Blum [330], data obtained in this connection on thick deposits are not directly applicable to thin coatings, such as are generally used in the chromium-plating industry [see, however, 444].
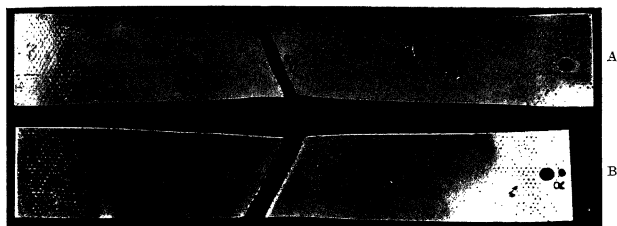
Tensile Test Pieces
A. Steel Strip } coated with
B. Brass Strip } Ni 25 μ, Cr 0·5 μ

FIG. 19.

(d) *Tensile Straining.* Adhesion may be tested by tensile straining of the work until cracking or peeling of the plating takes place. According to Faris [161], it is advisable to plate only a portion of the test bar.

Table IV shows the behaviour of materials A and B under tensile test; each of the values shown is the mean of three measurements (see also Fig. 19).

TABLE IV

TENSILE TESTS ON CHROMIUM-PLATED STRIP

Material.	Dimensions.		Y.P.	M.S.	Elongn. %	Behaviour of the Metal Coating.
	Width.	Thickness.				
A. Ni-Cr plated Mild Steel			33·0 kgm.² (21 tons/ in².)	39·3 kgm.² (24·95 tons/ in².)	33·5	No peeling of the plating on necking or at fracture.
B. Ni-Cr plated Brass	29·5 mm. (1·6 in.)	1·05 mm. (0·04 in.)	47·0 kgm.² (29·85 tons/ in².)	49·0 kgm.² (31·1 tons/ in².)	17·0	

No peeling of the plating was observed even after drastic extension of bar A (elongn. = 33·5 per cent.), indicating that the coating possessed good adhesive quality and capacity for deformation. No quantitative data could be obtained. Figs. 20–22 show sections of A after the tensile test, (α) at an unstrained, (β) at a slightly strained and (γ) at a heavily strained position. The unstrained point (α), which is near the grips, shows an amorphous structure (Fig. 20). The slightly strained point (β), in the region of the fracture, shows very clearly defined signs of deformation and of the formation of slip planes and incipient cracking. At the heavily strained position (γ), situated at the point of maximum necking, no cracking was visible under a magnifying-glass, but a magnification of 200 clearly revealed the existence of cracks. Figs. 23–25 show the coating on the brass sample B, at corresponding positions (α–γ); (α) shows an amorphous structure, and (β) a grained network; at (γ), the heavily strained position, isolated cracks and splits were observed.

(e) *Close-bend Test.* Up to the present, the most generally used method for determining adhesion has been the close-bend test, which has the primary advantage of simplicity. The strip is bent through an angle of 180°, round mandrels of progressively smaller diameter, until the two arms of the test piece are parallel: the diameter of the mandrel at which cracks or splits occur in the coating is taken as the measure of adhesion. Brook and Stott [237] describe a modified form of bend test which consists in twisting an 8 in. $\times$ $\frac{1}{2}$ in. strip at a uniform rate round a $\frac{1}{2}$-inch bar. (The relative value of bend and twist tests is dealt with at some length in discussion on this paper. Spiral twist tests have the advantage of determining adhesion over a larger surface area.)

In the present investigation, specimens of materials A and B were used. Fig. 26 shows the specimens after bending round a mandrel of 10 mm. (0·4 inch) diameter, and further flattening.

The ferrous-base specimen could be bent, without cracking of the coating, until one arm of the test piece lay in flat parallel contact with the other. In the brass-base sample, fine cracks appeared on bending round a mandrel of 2·1 mm. (0·08 inch). In view of the fact that the brass was in the cold-rolled condition, the presumption is that the cracking was due to brittleness of the basis metal, i.e. that the defects found in the coating were merely a continuation of cracks originating in the brass. Parallel tests made on uncoated samples of the steel and brass confirmed this assumption : the steel specimen could be bent round a mandrel of the same diameter as that causing cracking in the coated sample. (Figs. 27 and 28 show the condition of the coated and the uncoated samples at the positions of sharpest bend.) The tests confirm the influence of the basis metal on the behaviour of the coating, and emphasise the fact that results of tests

× 200
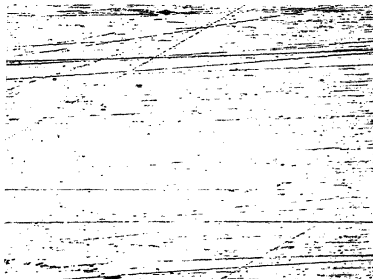
Tensile Test Piece, A.
Nickel-chromium-coated Steel.
Surface at γ (see Fig. 19).

Fig. 22.

× 200
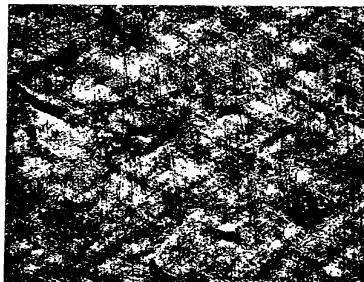
Tensile Test Piece, A.
Nickel-chromium-coated Steel.
Surface at β (see Fig. 19).
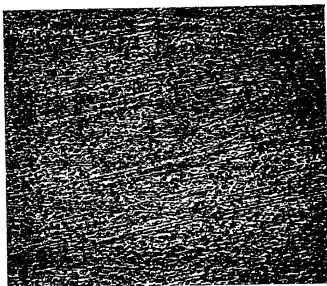
Fig. 21.

× 200

Tensile Test Piece, A.
Nickel-chromium-coated Steel.
Surface at α (see Fig. 19).

Fig. 20.

Tensile Test Piece, B.
Nickel-chromium-coated Brass.
Surface at x (see Fig. 19).

FIG. 23.

Tensile Test Piece, B.
Nickel-chromium-coated Brass.
Surface at β (see Fig. 19).

FIG. 24.

Tensile Test Piece, B.
Nickel-chromium-coated Brass.
Surface at γ (see Fig. 19).

FIG. 25.

60
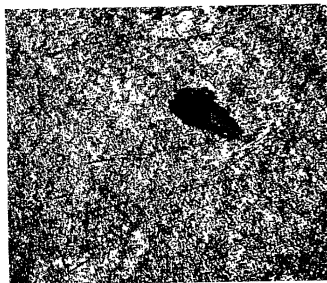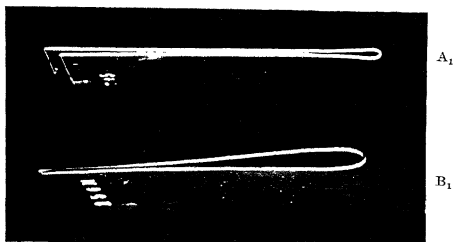
Close-bend Test Pieces
Steel Strip ⎱ coated with
Brass Strip ⎰ Ni 25 μ, Cr 0·5 μ
FIG. 26.

× 3

× 3
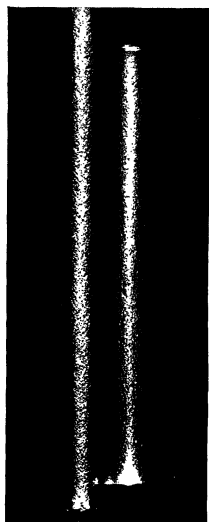
A   A₁   Close-bend Test Pieces.   B   B₁

A = Uncoated steel   B = Uncoated brass
A₁ = Nickel-chromium-coated steel   B₁ = Nickel-chromium-coated brass.
       Showing condition of specimens at points of sharpest bend.
    FIG. 27.   FIG. 28.

on coated materials are comparable only when the basis materials
are identical.

The thickness of the coating also affects the behaviour of electro-
deposits, but no extensive study has yet been made of this aspect of
the subject. It has been assumed that thicker plating would have a
greater tendency to crack on bending, due to the fact that the stresses
in the outer layers of heavy deposits would be higher than those in the
external layers of thinner coatings. According to Bablik [270], the
bending properties of galvanised coatings depend not so much on the
thickness of the coating as on the type and extent of the diffusion zone
formed between the basis and the coating metal. Rawdon [217] found
that in the case of galvanised sheet, thick coatings showed, on the
average, better properties than thin coatings.

(f) *Reversed Bend Tests.* Stress produced by reversed bending is
of a highly complex character. No data on the use of this type of test
for determination of adhesion are found in the literature. In the present
investigation, comparative alternating bend tests were carried out with
the nickel-chromium-plated materials A and B and with the correspond-
ing uncoated metals C and D.

The sharp fall in the bending values of the steel sample when
chromium-plated is noteworthy (see Table V). The electrodeposition
treatment had produced brittleness in the steel, presumably due to
occlusion of hydrogen [247, 444]. No parallel effect occurred in the
brass sample, in which cracking set in only immediately before fracture.
The cracks in this case originated in the basis material.

TABLE V

REVERSE-BEND TESTS ON COATED AND UNCOATED STRIP.

Material.	Dimension of Test Piece.		No. of Reverse Bends prior to	
	Width.	Thickness.	Cracking of the Coating.	Fracture of the Test Piece.
A. Mild Steel: Ni-Cr coated.			13	15
C. Mild Steel: uncoated . .	30 mm.	1·05 mm.	—	22
B. Brass: Ni-Cr coated . .	(1·2 in.)	(0·04 in.)	21	24
D. Brass: uncoated . . .			—	27

Fig. 29 shows the alternating bend test specimens A and B. Figs.
30 and 32 show the appearance of the surface at about 5 mm. (0·2
inch) from the point of fracture: it will be observed that the coating
shows marked evidence of deformation and incipient cracking. Figs.
31 and 33 show the appearance of the plating immediately at the

× 1

Reverse-bend Test Pieces.
A. Steel Strip ⎱ coated with
B. Brass Strip ⎰ Ni 25, Cr 0·5 μ
Fig. 29.

points of fracture.   Coarse cracks are observed on both samples, those
on the brass specimen gaping open especially widely.

   (g) *Deep-drawing Tests.*   Deep-drawing tests have been widely used
for determination of adhesion.   Rawdon [217], however, considers this
type of test less suitable for the purpose than the tensile or bend test.
Romanoff [534] also discusses the Erichsen test,[1] and gives details of
a modified cup test claimed to ensure accurate detection of faulty
adhesion.   Table VI gives the results of the Erichsen tests made in the
present investigation.

TABLE VI

DEEP-DRAWING PROPERTIES AS DETERMINED BY ERICHSEN CUPPING TEST

Material.	Width.	Length.	Thickness.	Depth of Cup.	Behaviour of the Coating.
A. Mild Steel (Ni-Cr coated)	70 mm. (2·76 in.)	150 mm. (5·9 in.)	1·03 mm. (0·04 in.)	10·5 mm. (0·4 in.)	No cracking prior to fracture.
B. Brass (Ni-Cr coated)				7·7 mm. (0·3 in.)	Fine small cracks formed prior to fracture.

   [1] " In the Erichsen test, the sheet metal is placed between a die and an annular
holder. In order that the metal may be able to flow, as in practice, the sheet
is not tightly clamped (a clearance of 0·002 inch is allowed). This clearance is
an essential feature of the Erichsen test. A round-nosed tool of definite shape

Reverse-bend Test Piece, A.
Nickel-chromium-coated Steel.
Surface at z (see Fig. 29).
Fig. 30.

Reverse-bend Test Piece, A.
Nickel-chromium-coated Steel.
Surface at β (see Fig. 29).
Fig. 31.

Reverse-bend Test Piece, B.
Nickel-chromium-coated Brass.
Surface at α (see Fig. 29).
Fig. 32.

64
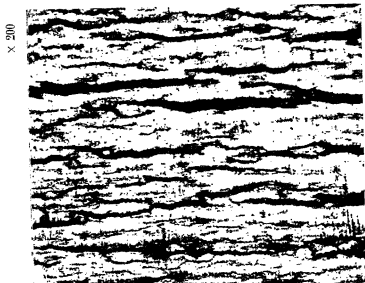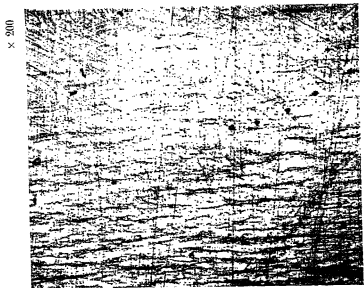
The fracture in sample A was in the form of a ring : no cracking was observed prior to fracture.   In the brass-base sample, fine cracks formed before fracture, at the point of maximum reduction in area : the cracks originated in the basis metal and are believed to be due to the brittleness of the hard-rolled brass (*vide supra*).

(*h*) *Ball-Indentation Tests.*   The methods of adhesion test discussed above, which are based on deformation of the basis metal, presuppose a foundation metal of high ductility.   Coatings deposited on brittle basis

× 200

Reverse-bend Test Piece, B.
Nickel-chromium-coated Brass.
Surface at β (see Fig. 29).
Fig. 33.

materials, e.g. castings, which are incapable of undergoing any considerable degree of plastic deformation without cracking, cannot be tested by such methods.   According to preliminary experiments made at the Bureau of Standards [330], the ball-indentation test appears promising for use in such cases.   This test is similar in type to deep-drawing, but the pressure involved confers additional strength on the metal of the coating.

In view of the extreme thinness of the sheet, a 2·5 mm. ball was used in the present tests, and, before testing, the sheet was folded so that it was exposed to test in a double layer.   Loads of 15·6, 30, 62·5,

is forced against the specimen by means of a screw, the rotation of which is transformed into a horizontal forward motion of the tool.   A cup is formed in the metal, and the depth of this cup, registered in millimetres when fracture occurs, is a measure of the drawing quality of the material.   The tool is shaped with sides sloping down to an end radius " (R. G. Batson and J. H. Hyde [328]).

See also a summary of the essential features of the Erichsen and other generally used forms of cupping test [557].

100, 150, 187·5 and 250 kg. were used. The coatings withstood the maximum load of 250 kg. without cracking or peeling either at the centre or edge of the ball impressions.

SUMMARY OF COMPARATIVE ADHESION TESTS ON EXPERIMENTAL STRIPS

All the samples behaved well under all types of adhesion test used. It is considered, however, that the methods described are unsuitable for *quantitative* estimation of adhesion, since they indicate only the ability of a given coating to adhere to the basis metal under a given degree of deformation. The nature of the demands made varies materially in the different types of test and it cannot, therefore, be anticipated that the results will be strictly and consistently comparable.

Adhesion Tests on the Automobile Components

Close-bend Tests. The close-bend method was selected for testing the majority of the automobile parts, and where the brittleness of the basis material precluded the employment of this method, the ball-indentation test was used.

All the samples could be bent parallel round a mandrel of 10 mm. (0·4 in.) without cracking or flaking of the coatings. After further flattening of the arms, cracking occurred at the respective internal bending radii (ri) shown in Table VII. In some cases flaking or peeling was also observed. The radii at which cracking occurred ranged from 0·75 to 4·25 mm.; the influence of thickness of sheet on bending properties is shown in column 10 of the table.

In general, the results indicate a good degree of adhesion : only J5, G13 and H gave low values. In the nickel-chromium-plated brass samples, peeling of the coating occurred on bending round a radius of 4·25 mm. In the copper-nickel-chromium-plated brass specimens G13 and H, bending radii of 4 and 3·3 mm., respectively, caused flaking of the coating. In all other cases bending round the radii shown caused only slight cracking, without flaking or peeling.

The greater brittleness of electrodeposited chromium, as compared with nickel, would presuppose a greater susceptibility to crack on close-bending, and the assumption is clearly confirmed by the form of the cracks in the respective specimens after the close-bend test. Fig. 34 shows the fine and branching cracks in the tough nickel plating of C2 (which gave a high bend value) and Fig. 35 the smooth, coarse cracks in the more brittle nickel-chromium-plated radiator shell M3.

Due to the lack of quantitative data on adhesion, no basis exists for assessing the relative value of the close-bend test. The results of the present tests yield no conclusive information with regard to the influence, on adhesion, of the nature of the basis metal, the character of the under-

TABLE VII.—CLOSE-BEND ADHESION TESTS ON AUTOMOBILE COMPONENTS

Basis Material	Exterior Coating	Component	Serial No.	Mark	Thickness of Intermediate Layers, μ. Copper	Nickel	Thickness of Exterior Coating, μ. Ni	Cr	Thickness of Sample, a, mm.	Bending Radius, r, mm.	Ratio $\frac{2r}{a}$	Bending Value $\frac{100a}{2r+a}$	Appearance of Coating at Point of Sharpest Bend.
Iron or Steel	Chromium	Radiator shell	4	E1	0·4	1·5		0·4	1·1	2·1	3·8	21	Fine cracks.
		Radiator shell	7	F1	0·2	8·0		0·7	1·15	2·55	4·4	18	„ „
		Shock absorber housing	8	G19	0·5	13·0		—	0·53	2·25	8·5	10	„ „
	Nickel	Lamp fitting	22	C2			8·0	0·5	0·85	1·5	3·5	22	Fine cracks.
		Radiator shell	25	G1		Nickel 2·5			0·64	2·13	7·9	11	Fine cracks and
		Badge	26	J5		2·5			1·8	4·25	4·7	17	Fine cracks and incipient peeling.
Brass	Chromium	Radiator screw cap	27	K11		2·5		0·4	0·53	1·5	5·7	15	Fine cracks.
		Ornamental hub cap	29	E7		3·5		0·3	0·62	1·38	5·3	16	„ „
		"Stop" lamp	30	G15		3·5		0·5	0·62	2·0	7·7	12	„ „
		Cable protection tube	31	J11		3·5		0·5	0·62	1·25	4·8	17	„ „
		Hub cap	32	M2		4·0		0·5	0·50	0·75	3·0	25	„ „
		Radiator shell	33	M3		4·0		0·4	0·85	2·75	6·5	13	„ „
		Footboard plate	34	F3		4·5		0·4	0·54	2·13	7·9	11	„ „
		Cap	36	J4		5·0		0·5	0·53	2·0	7·6	12	„ „
		Lamp casing	37	C3		5·0		0·5	1·1	2·3	4·2	19	„ „
		Radiator shell	39	N1		5·0		0·5	0·65	2·75	8·5	11	„ „
		Hub cap	40	N2		5·0		0·5	0·5	0·75	3·0	25	„ „
		Lamp cap	44	G3		14·0		0·7	0·55	1·7	6·2	14	„ „
	Nickel	Knob	46	G13	0·5	2·5	0·6		1·03	4·0	7·9	11	Fine cracks and slight scaling.
		Ornamental hub cap	47	G5	0·5	3·5	0·8		0·75	2·25	6·0	14	Fine cracks.
		Radiator shell	49	H	2·5	4·5	0·5		1·0	3·3	6·6	13	Fine cracks and slight scaling.

67

lays or the thickness of the coating.   In view of the fact that the basis
materials varied in chemical composition and structure and that the

Cracks formed during Close-bend Test.
No. 22 : C 2
μ; on Brass)
FIG. 34.

Cracks formed during Close-bend Test.
No. 33 : M 3
(Ni 4 μ, Cr 0·4 μ; on Brass)
FIG. 35.

conditions of deposition were different for the different samples,
any closely parallel relationship would be unlikely.

Ball-Indentation Tests. The parts tested by this method were chiefly castings, forgings and pressed parts of heavy section. A load of 3000 kg. and a ball of 10 mm. were used (see Table VIII). Calculations of Brinell hardness number from diameter of impression would in this case serve no useful purpose, since the values obtained would be an accurate gauge of the hardness neither of the plating nor of the foundation metal. The indentation test was here used merely as a criterion of ability of the coatings to withstand stresses similar in character to that imposed by deep-drawing.

Ferrous Samples. All the ferrous-base samples withstood the ball-indentation test without flaking or peeling of the plating (see Figs. 36–39).

In the nickel-plated sample C7, the edge of the impression remained free from cracks, whereas almost all of the chromium-plated specimens cracked at an equal or smaller diameter of impression. Of the chromium-plated samples, only the bumpers G6 and M1 remained free from cracks at the edge of the impression : in these cases, due to the high hardness of the basis metal, only very shallow impressions were made.

All the samples showed more or less marked cracking on the interior of the impressions. In C20, N3 and G10, the brittleness of the plating had caused it to splinter into small pieces.

The ball-indentation tests confirm the results of the close-bend test, showing the superior ductility of nickel plating.

No definite relationship could be established between the behaviour of the coatings in the indentation test and the nature and thickness of the intermediate coatings.

Brass Samples. The diameter of the ball impression varied from 5·9 to 7·0 mm. C5, which had a very thick intermediate layer of zinc, was the only sample giving a lower value. In all cases, more or less pronounced cracking occurred at the edges and on the interior of the ball impressions, but no flaking or peeling of the plating was observed. C4, which was directly chromium-plated with a heavier coating, showed numerous cracks over a considerable radius round the impression (Figs. 40 and 41). In the other samples, which carried thinner chromium coatings, deposited over underlays of other metals, cracks were observed only at the extreme edge and on the interior of the impressions.

Bronze Samples. Like the brass specimens, the bronze samples which had been directly chromium-plated showed numerous splits and coarse cracks, over a wide area round the ball impression (Figs. 42 and 43).

Zinc-base Die Castings. The nickel-plated door handle A1 showed fine cracks at the edge of the impression and some flaking of the

TABLE VIII

BALL INDENTATION TESTS ON AUTOMOBILE COMPONENTS

Basis Material	Exterior Coating	Component	Serial Number	Mark	Thickness of Intermediate Layers, μ		Thickness of Exterior Coating, μ		Diameter of Impression. mm	Appearance after Test.		Fig. No.
					Copper.	Nickel.	Nickel.	Chromium.		At Ridges of Impression.	At Centre of Impression.	
Iron or Steel	Nickel	Hub cap	1	C7	3·0	—	5·0	—	0·18	Free from cracks	Fine cracks	—
		Front-seat fitting	3	D3	—	5·0	—	0·4	5·90	Fine cracks	Fine cracks	—
		Cable protection tube	5	J11	0·2	4·0	—	0·5	6·17	Fine cracks	Fine cracks	—
		Gear handle	6	G11	0·2	7·0	—	0·6	5·53	,,	,,	—
		Lamp handle	9	G4	0·4	16·0	—	0·8	5·21	,,	,,	—
		Bonnet hinge	10	G18	0·5	22·0	—	0·9	6·09	,,	,,	—
		Lamp bracket	11	C50	0·5	25·0	—	0·5	6·03	,,	Coarse cracks	36
		Bonnet screw	12	F4	0·3	37·0	—	0·6	4·42	,,	Fine cracks	—
		Lamp cross-bar	13	N3	5·0	8·0	—	0·5	5·70	Coarse cracks	Coarse cracks	—
	(Chromium	Lamp adjusting arm	14	G10	Brass 5·0	Brass 5·0	—	0·5	6·13	Coarse cracks	Coarse cracks	—
		Closing disc	15	K4	Zinc Not determinable	Brass 5·5, Nickel 3·0	—	0·4	5·19	Fine cracks	Fine cracks	37, 38
		Cap	16	K2		Brass 3·5, Nickel 4·5			5·02	,,	,,	
		Wheel disc	17	K6		Brass 5·0, Nickel 5·0			5·50	,,	,,	
		Beading	18	K10		Brass 4·0, Nickel 8·0			4·96	,,	,,	
		Bumper	19	G6	Nickel 6·0, Copper 33·0	Nickel 38·0	—	0·5	3·25	Free from cracks	Fine cracks	39
		Bumper	20	M1	7·0, 7·0	2·0	—	0·75	2·80	,,	,,	—
		Running-board rail	23	C4	—		—	3·0	6·11	Cracked over a wide area round impression	Coarse cracks	40 41

Material		Part	No.	Code	Composition				Description	Description	Ref.
Brass	Chromium	Door handle	24	D1	Nickel 2·5		0·5	0·84	Coarse cracks	Coarse cracks	—
		Window adjuster	28	D4	3·5		1·0	0·88	Fine cracks	Fine cracks	—
		Bonnet support rail	38	C13	5·0		0·5	0·90	,, ,,	,, ,,	—
		Bonnet	44	K10	6·5		0·5	0·80	,, ,,	,, ,,	—
		Bonnet screw	43	K8	12·5		0·4	0·44	,, ,,	,, ,,	—
		Bonnet support rail	45	G8	25·0		0·8	0·21	,, ,,	,, ,,	—
		Ornamental hub cup	48	F2	Copper 0·4	Nickel 4·0	0·7	5·91	Fine cracks	Fine cracks	—
		Windscreen column	50	O17	0·3	4·5	0·6	5·83	Coarse cracks	Coarse cracks	—
		Bracing rod	51	J6	0·6	9·0	0·8	6·13	Fine cracks	,, ,,	
		Rail	52	C5	Zinc 120		0·5	5·14	Coarse cracks	Coarse cracks	—
Bronze	Chromium	Handle	53	B2			1·5	6·21	Coarse cracks over a wide area round impression	Coarse cracks	
		Steering-column bracket	54	B3			1·5	6·52	Fine cracks and flaking	,, ,,	42, 43
		Lock	57	B1			3·5	6·84		,, ,,	
	Nickel	Exterior door handle	58	A1			2·0	0·27	Fine cracks and flaking	Fine cracks	44 45
Zinc-base Die Castings		Exterior door handle	60	A2	Nickel 2·0		0·3	9·38	Fine cracks and flaking	Fine cracks and flaking	46 47
	Chromium	Radiator mascot	61	J1	Copper 0·5	Nickel 4·0	0·5	5·91	Fine cracks and flaking	Fine cracks and flaking	—
		Radiator screw cap	62	J9	0·4	2·5	0·6	6·40	,, ,,	,, ,,	—
	Nickel	Radiator screw cap	63	E2	Brass 0·8	Nickel 1·8	0·5	4·79	Fine cracks and flaking	Fine cracks and flaking	—
Aluminium Alloy Casting	Chromium	Bracket	65	J8	Nickel 4·0		0·4	6·94	Coarse cracks and splits	Splits; burnt effects on chromium plating	48 49

71

Cracks at Centre of Ball Impression.
No. 15 : K 4
(Brass 5·5 μ, Ni 3·0 μ, Cr 0·4 μ ; on Steel)
Fig. 38.

Cracks at Edge of Ball Impression.
No. 15 : K 4
Brass 5·5 μ, Ni 3·0 μ, Cr 0·4 μ ; on Steel)
Fig. 37.

Cracks at Centre of Ball Impression.
No. 11 : C 20
(Cu 0·5 μ, Ni 25 μ, Cr 0·5 μ ; on Steel)
Fig. 36.

72

× 200

Coarse Cracks formed at Centre of Ball
Impression.
No. 23 : C 4
(Cr 3 μ ; on Brass)

FIG. 41.

× 200
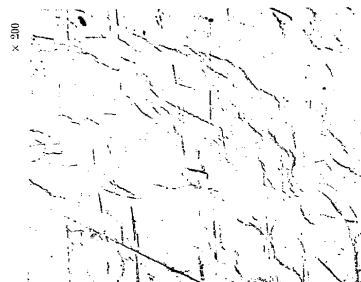
Cracking over wide area round Ball
Impression.
No. 23 : C 4
(Cr 3 μ ; on Brass)

FIG. 40.

× 100
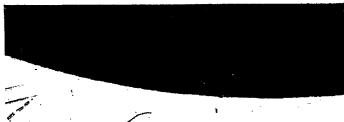
Edge of Ball Impression, free from
cracks.
No. 19 : G 6
(Ni 7 μ, Cu 0 4, Ni 33 μ, Cr 0·5 μ ; on Steel)

FIG. 39.

× 100

Fine Cracks and Flaking at Edge of
Ball Impression.

No. 58 : A 1

(M 2·0 μ ; on Zinc-base die casting)

Fig. 44.

× 200

Coarse Cracks at Centre of Ball
Impression.

No. 54 : B 3

(Cr 1·5 μ ; on Bronze

Fig. 43.

× 200

Coarse Cracks over a wide area round
Ball Impression.

No. 54 : B 3

(Cr 1·5 μ ; on Bronze)

Fig. 42.

74

× 200

Fine Cracks and Flaking at Centre of
Ball Impression.

No. 60 : A 2

(Ni 2 μ, Cr 0·3 μ ; on Zinc-base die casting)

Fig. 47.

× 100

Fine Cracks and Flaking at Edge of Ball
Impression.

No. 60 : A 2

(Ni 2 μ, Cr 0·3 μ ; on Zinc-base die casting)

Fig. 46.

× 200

Fine Cracks at Centre of Ball
Impression.

No. 58 : A 1

(Ni 2·0 μ ; on Zinc-base die casting)

Fig. 45.

coating (Fig. 44). In the centre of the impression, the coating showed
an all-over network of fine cracks (Fig. 45).

× 200

Splits at Edge of Ball Impression ("burnt" chromium).
No. 65 : J 8
(N4 μ, Cr 0·4 μ ; on Aluminium Alloy casting)
FIG. 48.

× 200
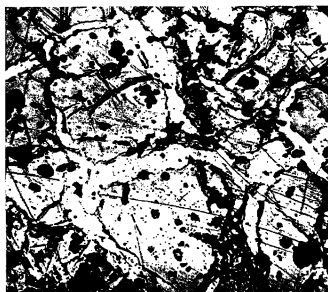
Coarse Cracks and Splits at Centre of Ball Impression ("burnt" chromium).
No. 65 : J 8
(Ni 4 μ, Cr 0·4 μ ; on Aluminium Alloy casting)
FIG. 49.

On all the chromium-plated samples, fine cracks and flaking had
occurred both at the edge and the centre of the impressions; typical
examples are shown in Figs. 46 and 47.

Aluminium Alloy Castings. On the one sample tested, J8, numerous splits of polygonal form were observed at the edge of the ball impression (Figs. 48 and 49), but the coating did not become detached from the base.

SUMMARY.

The results demonstrate the inadequacy of the ball-indentation test as a gauge of the adhesion properties of metal coatings, since coatings which adhere well to the base may behave badly under ball-indentation test, and, conversely, coatings which show poor adhesion do not necessarily exhibit any distinctive inferiority in the indentation

× 1

Coating on No. 9 : G 4, showing
poor adhesion.

(Cu 4 μ, Ni 16 μ, Cr 0·8 μ ; on Steel)

FIG. 50.
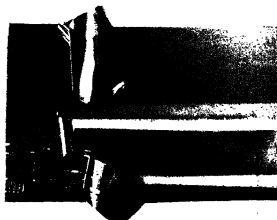
Coating on No. 19 : G 6, showing
poor adhesion.

(Ni 7 μ, Cu 6 μ, Ni 33 μ, Cr 0·5 μ ; on Steel)

FIG. 51.

test.[1] G4 and G6 showed good results in the indentation tests, but in both cases the coating could be easily separated from the base (Figs. 50 and 51). (See confirmatory conclusion, p. 178.)

The ball-indentation test is therefore primarily a test of the capacity of the coating for plastic deformation ; the results cannot be used as a general criterion of adhesive quality.

[1] See also 534.

HARDNESS AND WEAR RESISTANCE

Methods of Test [1]

Hardness and wear-resistance are of less vital importance in bright plating used on automobile parts than in thick coatings used on tools and machine parts for the purpose of protection against wear and abrasion.[2] Certain automobile parts, however, are subject in service to sliding friction, and it was therefore considered advisable to study the hardness and wear-resisting properties of the coatings under investigation.

It is generally known that the hardness of electrodeposited metals may vary within wide limits (Table III) [3] and that hydrogen content is a particularly important factor in this connection. Occluded hydrogen lowers the hardness of zinc, tin, lead and cadmium, but raises that of iron, nickel, silver, copper, chromium and many other metals.

Chromium is capable of absorbing up to 2000 times its own volume of hydrogen [4, 175 : see also p. 53] and chromium plating heavily charged with hydrogen may give off gas on the intermediate layers, causing increase in their hardness and producing embrittlement, with consequent lack of adhesion and mechanical strength in the coated product [444, 446 : see also p. 52]. Due to its high hydrogen overvoltage (see p. 96), copper would at first appear to be highly suitable for use as an underlay to chromium, but copper has a deleterious influence on the colour of the superimposed chromium and tends to lower its hardness and wear-resisting quality. The hydrogen overvoltage of nickel is considerably lower than that of copper, but the high hardness of nickel enhances the wear-resistance of the chromium coating, and for other reasons (vide pp. 140 and 211) nickel is universally regarded as the most suitable underlay. It is, however, important to avoid occlusion of a large amount of hydrogen in the nickel underlay,

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[1] For a comprehensive discussion of methods of hardness and wear-testing, see 69, 153, 244, 328, 467, 525, 536. See also papers dealing specifically with the testing of thin coatings referred to on p. 79.

[2] 50, 52, 53, 109, 118, 124, 161, 194, 323, 338, 346, 375, 420, 474, 533, 541, 542, 561, 582.

[3] 107, 123, 194, 201, 204, 220, 221, 258, 286, 287, 344, 345, 353, 367, 386, 438, 441, 455, 483, 553, 566, 577, 579, 582.

since nickel plating heavily charged with hydrogen is in a state of internal stress and is therefore liable to peel away from the base.

In determining the hardness of metal coatings, it is of primary importance to take into consideration the extreme thinness of the plating.[1] The tests used must operate on the surface only, as in the case of a sliding, polishing or abrading action.

Hardness and resistance to wear and abrasion have been the subject of an extensive literature (footnote, p. 78), but comparatively few investigations have dealt with these properties as exhibited by thin metal coatings [see, however, 164, 211, 251, 282, 346, 356, 372, 427, 458, 501, 517, 534, 566, 577]. According to Blum [387] no general relationships can be formulated between hardness and wear-resistance, and only an approximate evaluation of wear-resistance can be deduced from the results of scratch-hardness tests. H. K. Herschman [346], in testing chromium deposited on steel under varying conditions calculated to produce, respectively, " bright," " milky " and " frosty " deposits, found that, in spite of clearly defined variations in wear-resistance, no appreciable difference could be found in the scratch hardness of the respective samples. O. F. Hudson [445] concluded from a study of wear during polishing of platinum, palladium and brass, and nickel-, palladium-, and silver-plating that " the tests show very little relationship between the rate of wear and the Brinell or diamond hardness number : thus, two kinds of nickel plating, of which the ' hard ' had ·approximately double the hardness of the ' soft,' gave about the same rate of wear. The ' hard ' and ' soft ' kinds of palladium plating showed a small difference in the rate of wear in favour of the ' hard ' plating, but the difference was nothing like so great as the difference in hardness. Except in the very broadest sense that the hardest surface (platinum-plated) had the greatest resistance to wear (loss of thickness) and the softest (silver-plated) had the least, the hardness number of the materials tested cannot be taken as a guide to the wearing properties under conditions of polishing."

A brief summary is given below of some methods which have been used for determination of wear-resistance.

1. Testing by means of *Revolving Discs or Flat Surfaces moving backwards and forwards,* measurement being made of the amount of friction required to lay bare the foundation metal, or of the loss in weight of the specimens during abrasion. The results obtained by this

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[1] Macnaughtan and Hothersall [211], who consider that the Brinell test is more accurate and reproducible than either the scratch hardness or the scleroscope test, give a table showing the minimum thickness of deposit of various hardnesses which can be tested by the Brinell method with a 1 mm. ball and a 10 kg. load. See also later observations on hardness testing by the same authors [566], and literature on the testing of thin coatings referred to above.

method are subject to vitiation by the following variable factors : change in grinding surface, effect of grinding medium on degree of lubrication, change in attacking effect of grinding medium due to increase or decrease in quantity, and, in certain cases, occurrence of work hardening resulting from friction.

2. Testing by *Grinding*, time-to-wearing-through the plating being taken as the gauge of wear-resistance. The form of apparatus used in this test has been described in detail by H. C. Wolfe [372].

3. Mention must also be made of apparatus designed by the Bureau of Standards [346] and used by Herschman for determining the wear-resisting properties of chromium plating on gauges. Specially accurate control of pressure, lubrication, and other variables is obtained with this form of apparatus.

Hardness.[1]

The Martens scratch test was selected for use in the present investigation. The defects inherent in scratch testing, e.g. flowing of soft metals and chipping of hard surfaces, are recognised, but in this case these limitations were not of supreme importance, since the tests were made with the primary object of obtaining comparative rather than absolute values.

In the Martens apparatus the diamond point is ground to accurate rectangular form so that the width of the scratch is twice its depth. Due to the extreme thinness of the coatings, it was necessary to depart from usual practice, which is to determine the load producing a scratch of 10μ width. Preliminary experiments established that a load of 3 g. gave scratches which were strictly comparable ; all tests were therefore made with this load. Under constant test conditions, the reciprocals $\left(\dfrac{1}{S}\right)$ of the width of scratch S could be used as comparative values for the scratch hardness, H.

Resistance to Wear.[1] Fig. 52 shows the apparatus used. It consists essentially of two felt discs (30 cm. : 12 inches diameter : 5 cm. : 2·0 inches thick) fastened to a common shaft and electrically driven at a speed of 10m./min. (33 ft./min.). The test pieces are fixed in a holder (*a*), which presses them at a constant load (*a* + test piece + applied load = 100 g.) against the surface of the grinding disc. All samples were of identical size, with smooth and even surfaces, ensuring that the applied pressure per sq. mm. of grinding surface was identical

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[1] In the absence of standard symbols, the following designations have been arbitrarily adopted throughout the present work :

$$H = \text{hardness}$$
$$L = \text{loss in weight}$$
$$S = \text{width of scratch}$$
$$W = \text{wear value.}$$

in all cases at commencement of test. Change in the grinding surface during operation could not be prevented, but the results of the tests showed that it had but little effect on the value obtained. At regular intervals of $2\frac{1}{2}$ mins. a given quantity of abrasive paste (chromic oxide : petroleum paraffin :: 1 : 2) was evenly spread over the active surfaces of both grinding discs.

Given constant conditions of test, the wear-resistance (W) of the metal coatings was mainly a function of two factors, viz. (1) resistance to friction (as conditioned by the hardness and toughness of the material), which can be measured by loss in weight during grinding, and (2) thickness of coating, which affects the length of time to grinding-through.

The wear value L (decrease in weight in g. per 5 mins. grinding time) was obtained by weighing the samples before test and at 5-minute
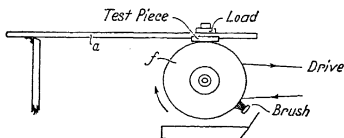
FIG. 52.—Wear-testing Apparatus.

intervals during grinding. In addition the time to grinding-through of the plating was calculated (Z).

In a preliminary series of tests, special attention was devoted to the discovery of any relationship which might exist between scratch hardness and resistance to wear. The results obtained (Table IX ; Fig. 53) lead to the following conclusions :

Increase in scratch-hardness (H) is accompanied by rise in wear-resistance (W), but the ratio H : W varies widely in different materials. Two samples of electrodeposited chromium, whose individual values for hardness and wear-resistance varied appreciably, showed substantially identical H to W ratios.

Birett [386], in a study of the influence of conditions of deposition on the hardness of electrodeposited chromium, found that hardness falls with rise of bath temperature, but increases with increase in current density, whereas the concentration of the bath, its acid content, the presence of impurities and the character of the cathode material appear to exert but little influence on the hardness and wear-resistance of the electrodeposit (see also studies of the influence of conditions of deposition on hardness referred to on p. 78).

TABLE IX

Scratch Hardness and Wear Resistance Properties of Metals and Alloys

Metal or Alloy.	Composition, Physical Condition, etc.	Scratch Hardness "H."		Wear Resistance "W."		Ratio $\frac{H'}{W'}$
		Width of Scratch S. with 3g. load, μ	Reciprocal Hardness Value $H' = \frac{1}{S}.1000$	Decrease in wt., L, per 5 min. grinding $\frac{1}{10,000}g$	Reciprocal Wear Value $W' = \frac{1}{L}.1000$	
Tin	As cast	20	50	41	24.4	2.05
Aluminium . . .	As cast	16.5	60.6	20	50.0	1.20
Silver	Fully annealed	14	71.4	66	15.1	4.73
Zinc	As cast	12	83.3	59	17.0	4.88
Aluminium casting alloy .	Cu 10.2, Ni 0.15% Si and Zn tr., Al remainder	10	100	54	18.5	5.40
Copper . . .	Annealed	9	111.1	38	26.4	4.21
Nickel silver . .	Ni 18, Zn 20% Cu rest	8.5	117.6	34	29.4	4.00
Zinc-base die casting alloy .	Zn 92-93% + Al and Cu	8.0	125.0	49	20.4	6.00
Bronze	Cu 85, Sn 5, Zn 7, Pb 3%	7.8	128.2	31	32.3	4.00
Brass	Half hard	7.5	133.3	29	34.5	3.86
Nickel	Rolled sheet	6.0	166.6	25	40.0	4.10
Mild steel . . .	Rolled sheet	5.2	192.3	12	83.3	2.30
Steel	1.25% C.	3.0	333.3	6	166.6	2.00
Chromium I . . .	Semi-hard electrodeposit	2.6	384.6	3.3	303.0	1.27
Chromium II . . .	Hard electrodeposit	1.6	624.2	2	500.0	1.25
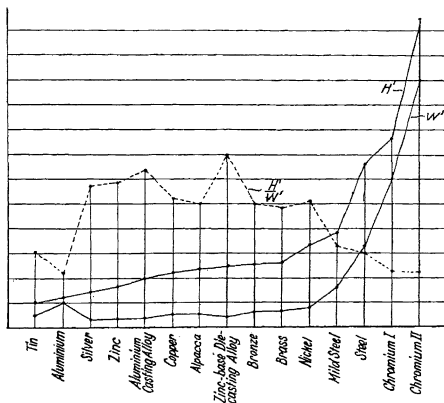
FIG. 53.—Scratch-Hardness and Wear-Resistance of Metals and Alloys.

Tests on the Automobile Components

Main Series of Tests. (Table X.) In spite of the very low load used (3 g.), satisfactory scratch-hardness values could be obtained on only a few samples, on which the thickness of plating was somewhat above the average. In by far the majority of cases, the width of scratch was more than double the thickness of the plating, indicating that the scratch had penetrated into the underlay. Samples to which this statement applies are shown in brackets in Table X. The test used for determination of wear-resistance, however, yielded comparable results even with thin coatings.

The nickel-plated samples (C7, C2 and A3) gave hardness figures (H′) of 217, 238 and 232 respectively (average 229) and wear-resistance values (W′) of 100, 100 and 83·3 (average 94·4), as compared with H′ = 166·6 and W′ = 40 for nickel sheet (Table IX). These figures indicate that electrodeposited nickel plating is considerably harder and more resistant to wear than rolled nickel.[1]

In the case of the chromium-plated samples, only G6, C4, B3, B4 gave values which could be used for comparison of scratch hardness with wear-resistance. The ratios $\dfrac{H'}{W'}$ are respectively 1·76, 1·27, 1·25

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[1] In rolled nickel the hardness and wear-resistance are materially affected by the degree of cold-working which the metal has undergone [566].

TABLE X.—SCRATCH HARDNESS AND WEAR RESISTANCE OF METAL COATINGS ON AUTOMOBILE COMPONENTS

1.	2.	3.	4.		5.		6.		7.		8.	9.		10.
Basis Metal.	Exterior Coating.	Component.	Serial Number.	Mark.	Thickness of Intermediate Layers, μ.		Thickness of Exterior Coating, μ.		Scratch Hardness, H.		Time required to grind through Coating, mins.	Wear-Resistance, W.		Ratio $\frac{H'}{W'}$.
					Copper.	Nickel.	Nickel.	Chromium.	Width of Scratch, 3g load, μ.	Reciprocal Hardness Value $H' = \frac{1}{S} \times 1000$, μ.		Decrease in Weight L per 5 mins. Grinding, $\frac{1}{10,000}$ g.	Reciprocal Wear Value $W' = \frac{1}{L} \times 1000$.	
Iron or Steel	Nickel	Ornamental hub-cap	1	C7	3·0	—	5·0	—	4·6	217·4	21	10·0	100	2·17
	Chromium	Front seat fitting	3	E1	—	5·0	—	0·4	(4·0)	(250)	3	3·0	333·3	(0·75)
		Radiator shell	4	E1	0·4	1·6	—	0·4	(3·8)	(264)	3	5·0	200	(1·32)
		Radiator shell	7	F1	0·2	8·0	—	0·7	(3·0)	(333·3)	3	3·0	333·3	(1·00)
		Wheel disc	17	K4	Zinc not determinable. Copper 7·0	Brass 5·0 Nickel 5·0	8·0	0·4	(3·4)	(294)	3	3·0	333·3	(0·89)
Brass	Nickel	Bumper	19	G6	Nickel 7·0	Copper 6·0 Nickel 33·0	5·0	—	1·7	588	3	3·0	333·3	1·76
		Bumper	20	M1	7·0	Copper 35·0 Nickel 2·0	—	—	(3·4)	(294)	4·5	3·0	333·3	(0·89)
		Lamp fitting	22	C2	—	—	—	—	4·2	238	12	10·0	100	2·98
		Running-board rail	23	C4	Nickel 4·0	Nickel 5·0	—	—	2·0	500	40	2·5	400	1·27
	Chromium	Radiator shell	38	M3	Copper 2·5	—	—	0·4	(2·5)	(400)	5	2·0	500	(0·80)
		Radiator shell	39	N1	—	—	—	0·5	(3·4)	(294)	2·5	3·0	333·3	(0·88)
Bronze	Chromium	Steering column bracket	40	H	—	—	—	0·5	(2·4)	(417)	4	2·5	400	(1·04)
	Nickel	Interior door handle	54	B3	—	—	—	1·5	1·6	624·4	15	2	500	1·25
		Interior door handle	56	B4	—	—	—	2·0	2·0	500	23	2	500	1·00
	Chromium	Exterior door handle	59	A3	Nickel 2·0	—	2·2	0·3	4·3	232·6	4	12	83·3	2·56
Zinc-base Die Casting	Chromium	Exterior door handle	60	A2	Nickel 4·0	—	—	0·3	(2·5)	(400)	4	5	200	(2·0)
Aluminium Alloy Casting	Chromium	Cover	64	J3	Nickel 3·0	—	—	0·5	(3·0)	(277)	0·5	5	200	(1·39)
		Bracket	65	J8	4·0	—	—	0·4	(2·8)	(358)	1·5	4	250	(1·40)

In the case of figures shown in brackets the width of the scratch was more than twice the thickness of the plating : the scratch had therefore penetrated into the underlay plating.

1·00 (mean 1·32) : the average value shows satisfactory agreement
with the figures shown for chromium in Table IX.

In general, the wear figures for the chromium-plated samples are
considerably higher than those of the nickel-plated specimens. The
average for the three nickel-plated samples is 94·4 ; for the fifteen
chromium-plated samples it is 343·3, giving a final chromium : nickel
ratio of $\dfrac{343·3}{94·4} = 3·64$.

The individual values for the chromium-plated samples vary over
a wider range than those of the nickel-plated specimens, due to variations
in conditions of deposition.

Coatings deposited on mild steel showed a generally lower degree
of wear-resistance than those plated on brass ; the lowest values
were given by zinc- and aluminium-base samples. E1 (mild steel,
chromium-plated over thin underlays of copper and nickel) also
showed very poor wear-resistance. The highest values were shown
by the heavy chromium plating deposited directly on bronze.

It would appear that, in addition to other factors operating in the
case of electrodeposited metals, hardness and wear-resistance are also
a function of the character of the basis metal and the nature of the
intermediate coatings. The indication is that if soft basis metals and/or
thick underlays of soft metals are used with only a thin overlay of nickel,
the chromium subsequently deposited will tend to be soft and show
poor resistance to wear.[1] Further experiments are required fully to
elucidate this point (see also comments on p. 5).

[1] See, however, data reported by Herschman [346] on wear-resistance of
copper-chromium-plated gauges.

RESISTANCE TO HIGH TEMPERATURE AND REVERSALS OF TEMPERATURE

Factors Influencing Behaviour of Metal Coatings

High-temperature conditions are seldom encountered in automobile service. Certain parts may be used at slightly raised temperature, but temperatures in excess of 100° C. occur only in the case of lamps, or during soldering or welding operations. From the service point of view, the behaviour of nickel- and chromium-plated parts under *alternations* of temperature is of much more vital importance.

Various physical properties of the basis and interlay metals play an important part in determining the response of the outer coating to such conditions:

Temperature of Melting-point. Table XI shows the melting-points of the metals and alloys under consideration. From a practical point of view, testing up to the temperature of the melting-points is unnecessary, but where resistance to raised temperature is required in plated parts it should be borne in mind that the properties of the basis metal have a bearing on the behaviour of the outer coating.

Transformations in the Solid State. Transformations in the solid state, which are associated with important changes in physical properties, also affect the behaviour of the coating. Copper, nickel and chromium undergo no transformations in the solid state : nickel has a magnetic transformation point at 340°–380° C. [288], but this change does not affect the mechanical properties of the metal.[1] The basis metals and alloys at present under consideration are stable, with the exception of aluminium-containing zinc alloys (see p. 54).

Mutual Diffusion of the Basis, Underlay and Coating Metals. The mutual diffusion capacity of metals is affected very materially by temperature. Practically speaking, diffusion of iron or nickel into chromium occurs only at temperatures above 1100° C. (2012° F.). [For data on the mutual diffusion capacity of iron, nickel, chromium, copper, see 120, 155, 225, 382, 395, 456, 457, 505, 511.]

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[1] Heat treatment has, however, a considerable effect on the mechanical properties of electrodeposited nickel [see 438].

Zinc, however, diffuses readily into iron, copper and copper alloys at relatively low temperatures [67, 137, 149]. Castell [494] gives a detailed discussion of this effect as related to the behaviour of copper-nickel-chromium-plated zinc-base automobile fittings, under conditions of atmospheric attack or raised temperature. In certain circumstances, a high mutual diffusion capacity between the metals of the base or underlay and the coating may lead to disintegration of the coating. Zinc is seldom used as an underlay.

TABLE XI

PHYSICAL PROPERTIES OF THE METALS AND ALLOYS USED AS BASES OR COATINGS *

Metal or Alloy.	Melting point ° C.	Coefficient of Thermal Expansion, 10^{-8} mm.	
		20°–100° C.	10°–250° C.
Chromium	1565 [1]	840	—
Nickel	1451 [2]	1300 [5]	— [5]
Copper [6]	1083	1650	—
Zinc	419·5	1410 ⊥ to } hex. 6390 ‖ to } main axis	—
60/40 brass [6]	905–890 [3]	—	1982 approx.
Bronze [6]	1016–887	—	1820 ,,
Mild steel	1480–1350 [4]	—	1260 ,,
Aluminium alloy (9% Cu) .	635–548	—	2300 ,, [8]
Zinc-base die-casting alloy[7]	430–385	—	—

* The values in the table are those given in the original report and used for comparative purposes in Table XXVI, p. 186. For further data on the melting-points and the thermal expansion of the respective materials see *International Critical Tables*, Vols. I and II [149], *National Metals Handbook* [424], and the individual papers referred to in the footnotes to the table.
  [1] Smithells [264] considers 1920° C. a minimum temp. for the m.p. of chromium. The point is variously placed by different investigators, e.g. Hoffmann and Tingwaldt [347] report 1800 ± 10° C. and 1765° ± 10° C. for different samples. Adcock [159] gives 1830° C. for very pure chromium. See also 302.
  [2] The Bureau of Standards [288] places the m.p. of nickel at 1455° C. [cf. 341].
  [3] The copper content of the brasses varied from 55·6 to 63·2 per cent. The temperature of commencement of solidification rises with increasing copper content [149].
  [4] The temperature of commencement of solidification rises with decrease in carbon content.
  [5] See also Bureau of Standards data [59 and 288].
  [6] See also data on the properties of copper and copper alloys summarised in the publications of the Copper Development Association [496].
  [7] Chase [495] gives a comprehensive review of the properties of zinc-base alloys.
  [8] See also 125.

Vapour Pressure (Saturation Pressure). The vapour pressure of most metals at working temperature is so low as to have no practical bearing on the behaviour of metal coatings under conditions of alternating temperature (see 149 and 168). Zinc, however, volatilises at a comparatively low temperature: at 333° C. (631° F.) the vapour

pressure is 0·00539 and at 500° C. (1049° F.) the value is 9·18. If resistance to high-temperature conditions is required in nickel- and chromium-plating, interlays of zinc should be avoided, since the adhesion of the plating to the basis metal may be deleteriously affected by volatilisation of the zinc layer.

Coefficient of Thermal Expansion. If the coefficients of thermal expansion of the basis and the coating metals differ greatly, rise in temperature and temperature reversals will cause stresses in the plating and at the edges of the metal layers and these stresses will lead to peeling and cracking of the plating.

Table XI shows that chromium has a very low coefficient of thermal expansion as compared with the metals and alloys used as basis materials. It should be noted that the values given in this table refer to *compact* metals and alloys. Just as the optical constants of very thin metal films differ from those of the corresponding metals in the compact form, so coefficients of thermal expansion of very thin electro-deposited nickel- or chromium-plating may, due to differences of structure or chemical condition (hydrogen content,[1] etc.) show values widely different from the coefficients of the corresponding metals in massive form.

Further, it must be remembered that rise of temperature and alternations of temperature impose drastic demands on the deformation capacity and adhesive power of thin chromium layers deposited directly on brass, bronze or aluminium. Intermediate coatings of metals whose coefficients of thermal expansion lie between those of chromium and the basis metal may be expected to have a compensatory influence on the stresses occurring in the chromium plating on rise of temperature. General opinion overwhelmingly favours the use of nickel as the under-lay metal, since its coefficient of thermal expansion is higher than that of chromium but lower than that of brass, bronze or aluminium (see also p. 187).[2]

Tarnishing at High Temperatures. A further property which vitally affects the practical value of metal coatings is their resistance to tarnish and oxidation at high temperatures.

[A very exhaustive discussion of tarnish films on metals, and related coloration [502], includes detailed reference to the literature of the subject. In this connection see also 85, 158, 227, 539, 563.]

Tests on Behaviour of Metal Coatings at High Temperatures

The object of this section of the investigation was threefold, viz. to determine the temperatures at which tarnishing sets in and the surface

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[1] The influence of hydrogen content on coefficient of thermal expansion of chromium is illustrated by experimental data cited by Blum [387].
[2] See 111.

of the plating becomes matt, to ascertain whether peeling or cracking of the plating occurs at high temperatures, and to determine to what extent the behaviour of the plating at raised temperature is affected by the types of basis metal used and the characteristics of the metal(s) used for the intermediate layers.

Specimens coated with various combinations, on various types of basis material, were heated under varying conditions of temperature and time, viz. 280°, 300°, 330°, 400°, 500°, 600° and 700° C. (536°, 572°, 626°, 752°, 932°, 1112°, 1292° F.) for $\frac{1}{2}$ hour and 5 hours. After heating, the test pieces were cooled in air and were examined, by both macroscopic and microscopic methods, with reference to lustre, colour and surface condition.

SUMMARY

Nickel plating.

C7, steel-base, copper-nickel-coated, showed no surface change after heating for 5 hours at 280° C. (536° F.) or $\frac{1}{2}$ hour at 330° C. (626° F.). A pale yellow tarnish colour first developed after 5 hours at 330° C. (626° F.), a result which is in satisfactory agreement with that reported by Tammann and Köster, who observed the first yellow coloration on nickel after 3 hours at 350° C. (662° F.). [See 419, 502.] The results lead to the conclusion that thin electrodeposited nickel films show approximately the same behaviour at high temperatures as massive nickel, and that an iron base and an interlay of copper have no appreciable influence on the conditions required to produce tarnishing.

After heating for 5 hours at 400° C. (752° F.) and 500° C. (932° F.), the nickel plating was still bright, but showed tarnish colours of various types. After heating at 600° C. (1112° F.) and 700° C. (1292° F.) it had become dark and matt and small crystals of oxide had formed on the surface. After 5 hours at 700° C. (1292° F.) the coating had begun to peel off.

From the metal content of a film of nickel oxide produced at high temperatures, Pilling and Bedworth [83] determined the composition of the oxide as NiO 90·3, Ni_3O_4 9·7 per cent.

Chromium plating.

Ferrous Samples. E1, copper-nickel-chromium-coated, showed no change in surface condition after 5 hours at 400° C. (752° F.). The first signs of yellow coloration occurred after $\frac{1}{2}$ hour at 500° C. (932° F.). Samples heated at 600° C. (1112° F.) and 700° C. (1292° F.) showed various forms of tarnish colour, but had preserved their lustre. After 5 hours at 700° C. (1292° F.) the plating became matt and began to peel away from the base (Fig. 54).

Comparison of the chromium- and nickel-plated samples indicates that under identical conditions, the temperature at which tarnishing sets in is about 150° C. (270° F.) higher for chromium than for nickel [cf. 155]. Chromium is therefore more suitable as a plating for lamps, since, although both metals have approximately the same degree of reflectivity, chromium retains its lustre longer than nickel.

K6, zinc - brass - nickel - chromium - coated, showed blisters after 5 hours at 500° C. (932° F.), see Fig. 55, whereas E1, without the zinc-brass parts of the underlay, was barely tarnished. The blisters on K6 were obviously due to the zinc and/or brass underlay, since zinc is the only one of the metals concerned which has so low a vapour pressure as to permit of volatilisation having occurred [364]. The results also indicate that the outer layers were porous or cracked. After 5 hours at 700° (1292° F.) the chromium coating was observed to be flaking off.

No. 4 : E 1
Copper-nickel-chromium
Coating; on Ferrous
Base.
After heating for 5 hours at
700° C. (1292° F.).
FIG. 54.

Brass Samples. After 5 hours at 400° C. (752° F.) sample H, copper-nickel-chromium-coated, showed green blisters, which increased in number and spread as the temperature of heating was raised (Fig. 56). After heating at 700° C. (1292° F.), clearly defined flaking of the chromium plating was observed. In this case also, the formation of the

× 2

| 400° | 500° | 600° | 700° C. |
| 752° | 932° | 1112° | 1292° F. |
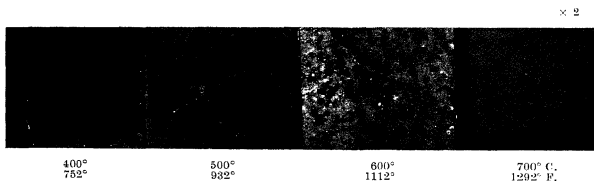
No. 17 : K 6 ; after heating for 5 hours at the temperatures shown.
Zinc-brass-nickel-chromium Coating ; on Steel.

FIG. 55.

efflorescent green patches may be associated with the zinc content of the brass base.

Bronze Samples. Sample B3, chromium-plated without underlay, behaved in a manner similar to H (*vide supra*), but the blisters were considerably more numerous. The first flaking occurred after 5 hours at 600° C. (1112° F.) (Fig. 56). The interlayers of copper and

nickel present on sample H appear to have exercised a protective
effect on the volatile zinc-containing foundation [cf. 364].

Zinc-base Die Castings. A2, nickel-chromium-plated, showed signs
of incipient melting after heating at 400° C. (752° F.) and this change
had resulted in sagging of the coating. After 5 hours at 400° C. (752° F.)
the surface had become very uneven and was tarnished to a brownish-
yellow; it had a blistered appearance and was partially disintegrated.
The experiments on this sample were abandoned at this point.

Aluminium Alloy Castings. After heating for ½ hour at 400° C.
(752° F.) the nickel-chromium-coated sample J3 showed a yellow tinge,
due to tarnishing of the nickel, which had been exposed at the cracks

×2

H

B 3

400°	500°	600°	700° C.
752°	932°	1112°	1292° F.
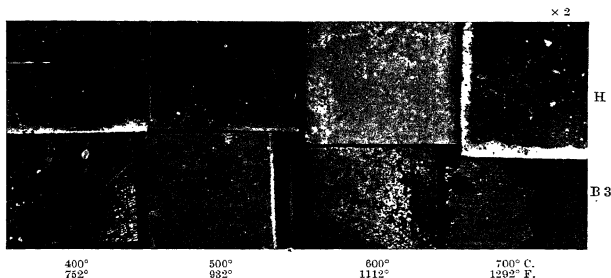
No. 49: H; Nickel-chromium Coating on Brass. after heating for 5 hours at
No. 54: B 3; Chromium Coating on Bronze the temperatures shown.

FIG. 56.

and pores on the chromium coating. After 5 hours at 400° C. (752° F.)
a yellow-grey coloration was observed, and the lustre was noticeably
impaired. After heating at 500° C. (932° F.) the surface had become
matt and brownish-grey in colour. At 600° C. (1112° F.) melting set in,
resulting in decomposition of the coating. The experiments were
abandoned at this juncture.

Tests on Behaviour of Metal Coatings under Alternations of Temperature

Repeated quenching tests were selected as the means of studying
the effect of interlays of metals having intermediate coefficients of
thermal expansion. The experiments were made on two directly-
chromium-plated samples and two samples chromium-plated over a
nickel underlay (Table XII).

The specimens were heated for 10 minutes at 300° C. (572° F.) and

TABLE XII

Serial Number.	Component.	Mark.	Basis Material.	Thickness of Nickel Underlay, μ	Thickness of Chromium Coating, μ.
23	Running board rail . . .	C4	Brass	—	3·0
54	Steering column bracket. .	B3	Bronze	—	1·5
25	Radiator shell	G1	Brass	2·5	0·5
39	Radiator shell	N1	Brass	5·0	0·5

quenched in water at room temperature ; the treatment was repeated 50 times. Before each heating, the samples were carefully dried, to avoid risk of peeling of the plating induced by volatilisation of water which might have penetrated into the pores of the coating. After each quenching, they were examined for signs of change in surface condition.

Fig. 57 (B3 ; bronze-base, directly chromium-plated, before test) shows the well-known amorphous structure of good bright-chromium-plating. C4, G1, and N1 were similar in appearance.

Figs. 58 and 59 show the condition of B3 and C4 (directly chromium-plated) after 50 treatments. The surfaces are covered with minute splits. In the heavily plated brass-base sample (C4) the cracks have joined up to form irregular polygons (Fig. 59) and other incipient cracks are also clearly visible. On the bronze-base sample, B3, which was plated with a thinner coating of chromium (Fig. 58), the cracks run in a smoother and straighter course. The formation of such cracks obviously lessens the protective power of the chromium coating. [In this connection see 192, 200, 204.]

Figs. 60 and 61 show G1 and N1 (chromium-plated over a nickel underlay), after test. Both specimens have remained free from cracks, the only marks visible on the surface being polishing scratches present before the quenching operations. Both specimens have a somewhat stained appearance, due to tarnish effects which were observed after 40 quenchings.

The tests show that chromium deposited over a nickel underlay is markedly less susceptible to deterioration under alternations of temperature than chromium deposited directly on the basis material, thus confirming the value of underlay of metals of intermediate coefficient of thermal expansion.

It must be emphasised that the drastic temperature changes (300° to 20° C. : 572° to 68° F.) used with the object of accelerating the test, would seldom occur in actual automobile service. Reversals of lesser magnitude would, in time, however, have a similar effect.

In view of the fact that a single treatment at 300° C. (572° F.) pro-

No. 23 : C 4

(τ 3·0 μ ; on Brass)

After 50 alternations of temperature.

Fig. 59.

No. 54 : B 3

(τ 1·5 μ ; on Bronze)

After 50 alternations of temperature.
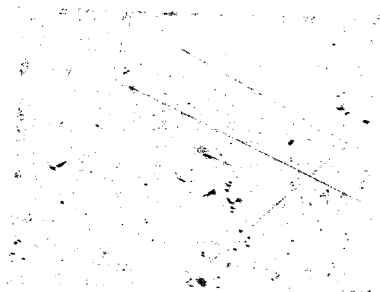
Fig. 58.

No. 54 : B 3

(τ 1·5 μ ; on Bronze)

Before quenching test.

Fig. 57.

93
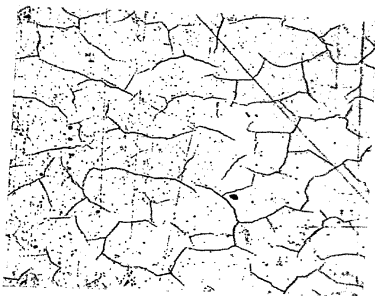
duces no change in surface condition of chromium plating, many
plating establishments regularly heat-treat chromium-plated articles
at this temperature in order to expel hydrogen.[1]   When this treatment
is used, care should be taken to avoid too rapid a rate of cooling.

× 200
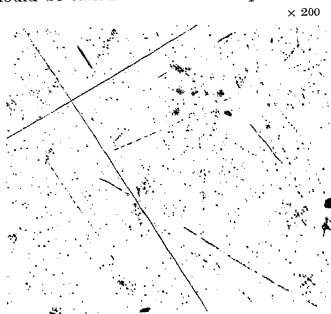
No. 25: G 1
(Ni 2·5 μ, Cr 0·5 μ ; on Brass)
After 50 alternations of temperature.
FIG. 60.

× 200
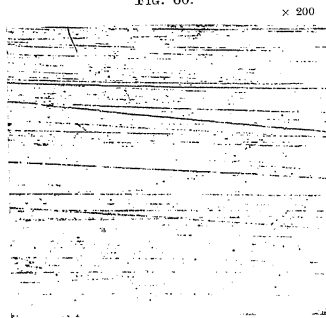
No. 39: N 1
(Ni 5 μ, Cr 0·5 μ ; on Brass)
After 50 alternations of temperature.
FIG. 61.

[1] For data on the effect of heat treatment on hydrogen content, adhesion,
porosity, wear- and corrosion-resistance, cracking and other properties of electro-
deposited chromium or nickel, see 63, 120, 312, 316, 331, 346, 348, 375, 438, 444,
485, 566, 580.

POROSITY

General Observations

Viewed from the strictly electrochemical standpoint, chromium coatings, whether used alone or in conjunction with underlays of nickel or copper, can be regarded as conferring protection on the less noble metals iron, brass, zinc, aluminium, only if the coating is completely dense and impervious. Even minute areas of porosity serve as starting-points for progressive corrosion.

Corrosive media act not only in the purely chemical sense, by penetrating through the pores of the coating and dissolving away the underlying metal, but also give rise to the formation, at the porous areas, of local elements which accelerate the corrosive attack, the less noble metal becoming the soluble electrode [571]. The attack proceeds underneath the coating, and the cohesion between the basis metal and the coating is gradually broken down. The increase in volume due to the corrosion products formed has a disintegrating effect and eventually the coating begins to peel away from the base. Other factors also influence the protective value of metal coatings, e.g. the physical characteristics of the metal deposited, and its adhesive qualities, but porosity rating may be regarded as the most reliable criterion of general protective value.

Porosity is caused primarily by gas bubbles which are formed by evolution of hydrogen during deposition.[1] [Mechanical injury of the surface, cracking caused by thermal stresses, peeling resulting from bending stresses, and certain other factors may also have a contributory influence.] Conditions obtaining during deposition of chromium are particularly adverse in this respect, since 80–90 per cent. of the current output is expended in generation of hydrogen. Cracks, non-metallic inclusions, and particles of other metals and oxides in the basis material all predispose to lowering of the hydrogen overvoltage and to localised evolution of gas [204]. Similar effects may be produced by the

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[1] Macnaughtan [212] describes the phenomena of " pinholing " and of " pitting," and discusses the influence of the respective defects on the porosity of the finished coating: see also 250, 331.

presence of solid matter in the electrolyte, e.g. basic salts, organic substances, dust, or particles of carbon from the anode [212, 315, 455].

Metals on which chromium is deposited should be those which have a hydrogen overvoltage higher than that of chromium.[1] Iron has a lower overvoltage than nickel or copper, and chromium deposited on iron therefore shows a greater tendency to porosity [336]. Copper has a higher overvoltage than nickel,[2] and would for this reason appear to be more suitable for use as an underlay to chromium : from other considerations, however (see pp. 140, 211), nickel is preferred as pre-eminently suitable for this purpose.

The high current densities which are now in such general use tend to cause increased evolution of hydrogen, the coating becomes porous and, due to absorption and occlusion of hydrogen, the plating becomes brittle and cracked. Birett [329] found 100 pores per sq. dm. in nickel plating 25μ thick deposited on iron at high current densities, as compared with 10 pores per sq. dm. on deposits made at low current density.

In addition to hydrogen bubbles, bubbles of air may be entrapped at the cathode when the electrolyte is operated at raised temperature, and oxygen evolved at the anode may be carried over to the cathode [9, 134, 212]. The ability of the gas bubbles to detach themselves from the cathode is affected by viscosity, surface tension and the composition of the electrolyte [212, 455, 506].

In order to overcome the porosity inevitably resulting from the conditions of deposition, it is usual to make the coatings of such thickness that pores which may be formed during the early stages of deposition are covered over by layers subsequently deposited [213]. For practical reasons, however, unlimited increase in thickness is undesirable and uneconomic : moreover, in the case of chromium coatings, thick deposits tend to crack and flake off [192, 204, 221]. There is, therefore, an optimum thickness of coating for obtaining maximum freedom from porosity. This optimum value is a function of conditions of deposition. With a bath temperature of 45° C. (113° F.) Baker and Rente [192] determined the optimum as 0.5μ. (0.00002 in.) ; Blum, Barrows and Brenner [331] found that for higher temperatures the optimum thickness was less clearly defined.[3]

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[1] For a very complete discussion of overvoltage, see 32, 72, 284, 484 ; see also 21, 28, 38, 87, 106, 135.

[2] The process of coating a steel article first with nickel, then with a thick coating of copper and finally with a deposit of nickel, has been recommended for reducing porosity in nickel deposits [90, 133, 212].

[3] The recent American exposure tests [485] indicate that " from 0.00001 to 0.00003 inch of chromium is a critical range, in which a slight variation in thickness (or perhaps in the conditions of deposition) may either increase or decrease the protective value." The results also " suggest the advisability of relatively thick chromium deposits for very severe conditions, especially in an industrial atmosphere containing sulphur dioxide." See also summary, p. 220.

The causes of the stresses occurring in chromium plating and the means for their avoidance were discussed in detail in the chapter dealing with adhesion (p. 51). The factors which operate in favour of sound and dense deposits are : high bath concentration, raised temperature, agitation of the bath, low current density. Baker and Rente [192] found that a temperature of 55° C. (131° F.) gave the soundest plating, while Blum, Barrows and Brenner [331] give the optimum temperature as 65° C. (149° F.) , with current density 35 amps. per sq. dm. (329 amps. per sq. ft.).

In view of the difficulty of producing thick deposits of chromium which are both bright and sound, it is usual to deposit an underlay of other metal(s), followed by a thin coating of chromium. As will be shown later, the use of intermediate layers reduces porosity to an extent in excess of that which would be anticipated from the additive effect of the individual layers used (see pp. 118, 128, 193).

The Relative Position of the Metals in the Electrochemical Series : Determinations of Potential

Since metal coatings are seldom entirely free from porosity, the relative positions of the basis and coating metals in the electrochemical series is a matter of some importance [295]. Before proceeding to a study of porosity, therefore, determinations were made of the mutual electrochemical relations of the various metals. The conditions used in the determinations are shown in Table XIII. Readings were taken immediately after insertion in the electrolyte, and after 1, 5, 24 and

TABLE XIII
POTENTIAL MEASUREMENTS
(1% Sodium Chloride Solution: 24°–26° C. (75°–80° F.))

No.	Metal or Alloy.	Potential against Normal Calomel Electrode : volts, after				
		0 hrs.	1 hr.	5 hrs.	24 hrs.	120 hrs.
1	Zinc	− 1·02	− 1·06	− 1·08	− 1·07	− 1·04
2	Zinc-Die Casting Alloy	− 1·01	− 1·01	− 1·02	− 1·02	− 1·02
3	Aluminium Casting Alloy	− 0·69	− 0·69	− 0·71	− 0·70	− 0·68
4	Iron	− 0·40	− 0·55	− 0·65	− 0·70	− 0·65
5	Brass	− 0·22	− 0·21	− 0·22	− 0·24	− 0·22
6	Copper	− 0·19	− 0·20	− 0·21	− 0·22	− 0·21
7	Bronze	− 0·20	− 0·21	− 0·22	− 0·20	− 0·19
8	Nickel (commercial)	− 0·30	− 0·24	− 0·22	− 0·19	− 0·18
9	Nickel (electrolytic)	− 0·30	− 0·25	− 0·19	− 0·18	− 0·16
10	Chromium (commercial)	− 0·34	− 0·38	− 0·40	− 0·42	− 0·26
11	Chromium (electrolytic)	− 0·36	− 0·34	− 0·27	− 0·18	− 0·11

120 hours in a non-agitated solution. In Table XIII the metals and alloys are arranged in order of their electrochemical positions, as indicated by readings taken after 120 hours.

Conclusions. Zinc, zinc-base alloys, aluminium alloys and iron show the highest negative values : brass, bronze, copper and nickel are appreciably more noble and about equally negative. Immediately after insertion in the electrolyte, electrodeposited chromium, which is very pure, shows a potential considerably less noble than that of brass, bronze, copper and nickel, but after some time progressive passivation takes place and the final value indicates chromium as being nobler than the other metals. (See also p. 99.) The differences in potential between these metals are therefore not very considerable. Bauer and Vogel [42] make the following observations on the anomalous behaviour of chromium : " The initial value, which is quite low, gradually rises : even after 120 hours it was found impossible to obtain a stationary state such as occurs with most metals at some stage." To explain this behaviour Bauer and Vogel assume the occurrence of an oxygen electrode, which forms only gradually, as a result of the action of the atmospheric oxygen dissolved in the electrolyte. With chromium this action is progressive and the potential continues to rise gradually, without interruption, forcing itself up to the much nobler potential of oxygen. In commercial chromium, which is of a lower degree of purity, passivation appears to take place much more slowly ; after 120 hours the potential of the commercial chromium sample was still less noble than that of copper, bronze and nickel.

In a further series of experiments, one of the test metals was used as the reference electrode, in order to determine the corrosion-resisting properties of the interlay metals when in contact with the metals forming the coating(s) or foundation(s). The results (Table XIV) show good agreement with the measurements made against the normal calomel electrode (Table XIII).

Conclusions. Zinc is the least noble material against all the metals tested.

Iron is less noble than chromium, nickel, copper, brass.

Brass is somewhat more noble than chromium, but rather less noble than nickel and copper.

Bronze is more noble than chromium, brass, nickel and copper, but the difference in potential lies very close to the zero value.

Zinc-base alloys are very closely akin to zinc, i.e. considerably less noble than any of the other metals.

Aluminium alloys are less noble than chromium, brass, nickel and copper, but the difference in potential is not so great as in the case of the zinc-base materials.

Chromium shows a somewhat less noble potential than nickel and

TABLE XIV

POTENTIAL MEASUREMENTS

(1% Sodium Chloride Solution 24°–26° C. (75°–80° F.))

Electrodes.		Difference in Potential : volts, after			
Standard.	Measured against	0 hrs.	5 hrs.	24 hrs.	120 hrs.
Iron	Chromium	+ 0·18	+ 0·25	+ 0·24	+ 0·27
	Nickel	+ 0·34	+ 0·45	+ 0·40	+ 0·47
	Copper	+ 0·38	+ 0·43	+ 0·51	+ 0·47
	Brass	+ 0·37	+ 0·42	+ 0·44	+ 0·45
	Zinc	− 0·39	− 0·44	− 0·32	− 0·33
Brass	Chromium	− 0·16	− 0·19	− 0·14	− 0·08
	Nickel	− 0·01	+ 0·03	+ 0·04	+ 0·02
	Copper	+ 0·05	+ 0·02	+ 0·04	+ 0·08
	Zinc	− 0·78	− 0·79	− 0·78	− 0·79
Bronze	Chromium	− 0·18	− 0·23	− 0·18	− 0·14
	Nickel	− 0·05	− 0·02	− 0·03	− 0·04
	Copper	− 0·01	− 0·03	− 0·04	− 0·05
	Brass	− 0·02	− 0·05	− 0·03	− 0·03
	Zinc	− 0·83	− 0·84	− 0·84	− 0·86
Zinc-base Die Casting Alloy	Chromium	+ 0·60	+ 0·57	+ 0·66	+ 0·74
	Nickel	+ 0·79	+ 0·80	+ 0·81	+ 0·76
	Copper	+ 0·81	+ 0·78	+ 0·75	+ 0·72
	Brass	+ 0·76	+ 0·76	+ 0·74	+ 0·70
	Zinc	− 0·01	− 0·02	− 0·01	− 0·02
Aluminium Casting Alloy	Chromium	+ 0·38	+ 0·27	+ 0·42	+ 0·49
	Nickel	+ 0·46	+ 0·48	+ 0·49	+ 0·49
	Copper	+ 0·50	+ 0·48	+ 0·51	+ 0·54
	Brass	+ 0·46	+ 0·48	+ 0·47	+ 0·47
	Zinc	− 0·31	− 0·34	− 0·32	− 0·32
Chromium	Nickel	+ 0·11	+ 0·19	+ 0·21	+ 0·16
	Copper	+ 0·22	+ 0·24	+ 0·20	+ 0·22
	Zinc	− 0·60	− 0·57	− 0·55	− 0·62
Nickel	Copper	− 0·11	+ 0·03	+ 0·02	+ 0·05
	Zinc	− 0·78	− 0·83	− 0·81	− 0·79
Copper	Zinc	− 0·82	− 0·80	− 0·83	− 0·82

copper. (The present series of tests further demonstrates the anomalous behaviour of chromium referred to above.)

The results indicate that chromium plating deposited directly on iron, zinc, zinc-base alloys or aluminium alloys will. if it is porous, very seriously accelerate corrosion of the basis materials. The potentials of brass, copper and nickel are, as a rule, so close to that of chromium that no very substantial compensatory effect can be anticipated from

the use of these metals as interlays unless the coating is free from porosity.

In a third series of electrochemical tests, determinations were made on sections cut from the automobile components. Cut surfaces and unplated areas were protected by a coating of paraffin wax. Table XV gives the test conditions and results.

Conclusions. A2 (nickel-chromium-plated zinc-base die casting) and J8 (nickel-chromium-plated aluminium alloy casting), gave respectively the same low values against the normal calomel electrode as the uncoated zinc- and aluminium-base alloys (Table XIII, Nos. 2 and 3), indicating that in spite of the nickel underlay the coating was unsound. The ferrous samples D3 and E1, plated with 0.4μ chromium, over thin underlays of nickel, also showed values very close to that of the uncoated steel (Table XIII, No. 4). In all these cases, therefore, the protective effect of the coating had been incomplete.

In F1 and M1, which had thicker coatings of chromium (M1 had also a considerably thicker underlay of copper and nickel), the potential values were noticeably higher, as was that of the brass-base sample C5, which had a zinc underlay and a 0.5μ coating of chromium.

SUMMARY.

The results of the experiments indicate that reliable conclusions regarding soundness of electrodeposited chromium plating and of underlay coatings can be deduced from direct potential measurements only if the basis metal is considerably less noble than the metal of the coating, e.g. zinc, brass, aluminium. If the difference in potential is only slight, such measurements yield no conclusive information.

Tests for Determination of Porosity

The methods generally used to test porosity of metal coatings are based on the reaction of selected indicators with the ions of the basis (or underlay) metal(s) going into solution at the pores of the outer coating. (A useful summary of the subject is contained in the following papers : 295, 331 and 458 ; see also 228 and 391.) Attention may also be directed to a hot-water test [405 and 565], worked out primarily for use on tin coatings, but applicable, with certain minor modifications, to coatings of nickel, copper and chromium.

The first requirement for an indicator is that it shall contain a reagent which leaves the metal of the outer coating unattacked, but penetrates through the pores and reacts with the basis metal and/or the metals of the intermediate layer(s). The reagent may act in a purely chemical or in an electrochemical sense, the basis metal becoming the soluble electrode, i.e. the anode, and the coating the cathode.

TABLE XV

POTENTIAL MEASUREMENTS ON CHROMIUM-PLATED AUTOMOBILE COMPONENTS.

(1% Sodium Chloride Solution : Room Temperature)

Basis Metal.	Component.	Serial Number.	Mark.	Type and Thickness of Coating, μ.	Potential against Normal Calomel Electrode : volts after 1 day.	2 days.	5 days.	25 days.
Zinc Base Die Casting	Exterior door handle	60	A2	Nickel 2·0, Chromium 0·3	− 0·90	− 0·99	− 0·98	− 1·02
Aluminium Alloy Casting	Bracket	65	J8	Nickel 4·0, Chromium 0·4	− 0·61	− 0·64	− 0·65	− 0·65
Iron or Steel	Front seat fitting	3	D3	Nickel 5·0, Chromium 0·4	− 0·31	− 0·40	− 0·48	− 0·51
	Radiator shell	4	E1	Copper 0·4, Nickel 1·5, Chromium 0·4	− 0·37	− 0·50	− 0·52	− 0·51
	Radiator shell	7	F1	Copper 0·2, Nickel 8·0, Chromium 0·7	− 0·30	− 0·32	− 0·31	− 0·35
	Bumper	20	M1	Nickel 7·0, Copper 35·0, Nickel 2·0, Chromium 0·75	− 0·14	− 0·19	− 0·21	− 0·24
Brass	Rail	52	C5	Zinc 120, Chromium 0·5	− 0·17	− 0·26	− 0·29	− 0·30
	Running-board rail	23	C4	—, Chromium 3·0	− 0·25	− 0·13	− 0·14	− 0·14
	Lamp casing	44	G3	Nickel 14·0, Chromium 0·7	− 0·17	− 0·18	− 0·15	− 0·17
Bronze	Steering-column bracket	54	B3	—, Chromium 1·5	− 0·24	− 0·12	− 0·13	− 0·13

The following types of solution may be used :

1. Reagents which are sensitive to the metal ions passing into solution and which produce clearly defined precipitation or coloration.

2. Reagents which are easily reduced by the hydrogen evolved during solution of the metal and which thereby lose their colour or become characteristically coloured.

3. Dyes which are suitable for determination of hydrogen ion concentration (pH).[1]

In order to produce a localised and sharply defined reaction, the indicator solutions are made highly viscous by the addition of agar-agar or gelatin, and are used at raised temperature. To assist rapid cooling and gelatinisation, only a very thin coating of the indicator solution is applied. If the print method is used, in which a filter paper saturated with the indicator solution is applied to the plated surface, the addition of agar-agar or gelatin is unnecessary. Alternatively, a paper coated with gelatin may be used. Pitschner [177] recommends saturating the paper with the solution containing agar-agar, drying the paper and re-moistening it before test.[2] Vopel [185] prepares an indicator paper in the same way, using a well-filtered solution containing 200 c.c. alcohol, 18 g. gelatin, 20 g. sodium chloride, 2 g. ferricyanide, 800 c.c. water.

The number of pores over a given surface area is taken as the measure of porosity. C. T. Thomas and W. Blum [134] use as the figure of merit the quotient obtained by division of the number 100 by the number of pores found in a circle of 2 inches (5 cm.) diameter.

Ferrous Samples. The Cushman and Gardner ferroxyl indicator (sodium chloride 1 g., agar-agar 1–2 g., potassium ferricyanide 0·1 g., per 100 c.c. water) may be used for testing porosity of coatings deposited on a ferrous base [11, 12, 15, 16, 128, 140, 267]. It is desirable to use fresh solutions, but if prepared in the dark, the indicator remains stable for several days. Since iron has a potential lower than that of the chromium-plating or the copper or nickel underlay, the ferrous base becomes the anode, and the porous areas at which the iron goes into solution take on a blue coloration, as the result of the production of ferrous ions and the formation of Turnbull's blue, according to the formula :

$$K_3[Fe(CN)_6] + FeCl_2 = KFe[Fe(CN)_6] + 2 KCl$$
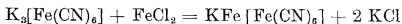
According to E. Müller [37] the empirical composition of the blue compound depends upon the ratio in which the components $FeCl_2$ and

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[1] For a description of the mode of action of indicators of types 2 and 3, see 284.
[2] See also note on p. 123, modifications proposed by Ollard [215] and Macnaughtan and colleagues [295 and 405], and conclusions drawn by Strausser and co-workers in relation to optimum conditions of test [537].

$K_3[Fe(CN)_6]$ are present in the solution ; as a rule, it is a mixture of alkali ferric-ferrous cyanides.

Preliminary experiments were carried out with sections from the radiator shell F1 (copper 0·2, nickel 8, chromium 0·7 μ). Fig. 62 shows a sample which, after cleaning with alcohol, had been treated by pouring over it a hot solution of the above reagent. The edges are surrounded with plasticine to prevent escape of the liquid. The photograph, taken $\frac{1}{2}$ hour after application of the indicator solution, shows that the marks produced by reaction at the pores had already begun to spread and blur, although the solution had been rapidly cooled. During the few hours following the test, the blurring became more pronounced.
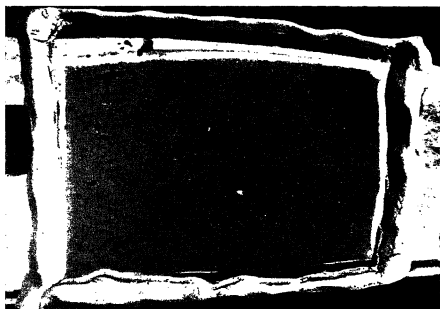
No. 7 : F 1
Copper-nickel-chromium Coating, on Ferrous Base.
After treatment by pouring ferroxyl indicator solution over surface.
FIG. 62.

Pitschner [177] recommends replacing about 20 per cent. of water by ethyl alcohol, in order to increase the viscosity of the solution and the hardening capacity of the film. The present authors, however, found that this modification produced no substantial improvement in definition or durability of the film.

Fig. 63 shows another method of making the test [263]. In this case the reagent used for attacking the iron was not added to the indicator solution, but the metal coating, prior to treatment, was pickled by being smeared over with a pad of cotton-wool saturated with a 3 per cent. solution of sulphuric acid. A solution containing 100 c.c. water, 10 g. gelatin, 2·5 g. glycerine and 0·1 g. potassium ferricyanide was then poured over the sample. The resulting definition was clearer than that

obtained in the previous test and the film was more stable. This
treatment is not to be recommended, however, since the sulphuric acid
pickle attacks the chromium plating and also the nickel and copper
underlays, and may therefore extend pores of only slight depth through
to the basis metal, giving results which indicate a higher degree of
porosity than is actually present.

× 1
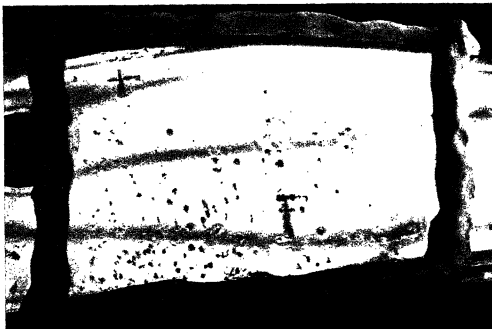
No. 7 : F 1.
Copper-nickel-chromium Coating, on Ferrous Base.
Etched with 3% sulphuric acid and subsequently treated by pouring ferroxyl indicator solution
over surface.
FIG. 63.

The various indicator paper methods are simpler in application, in
that there is no necessity to surround the specimen with plasticine to
prevent escape of liquid.

Fig. 64 shows a test paper from sample F1. In this case the filter
paper was saturated with an aqueous solution containing sodium
chloride 20 g., potassium ferricyanide 1 g., per 100 c.c. water, applied for
5 minutes to the test piece and subsequently rinsed. The impression
gives a clear definition of porosity. In comparing Fig. 64 with 63
and 62, it must be remembered that the indicator paper method gives a
mirror image of the specimen.

Fig. 65 shows the results of a test made with the same solution, but
with photographic gaslight paper covered with gelatin film. Gelatin
paper has the peculiar advantage of fitting into close contact with the
surface of the specimen, and therefore shows up even the smallest pores,
whereas ordinary filter paper lies somewhat unevenly on the surface.
Impressions made on gelatin paper, however, tend to blur, which may

No. 7: F 1. Copper-nickel-chromium Coating, on Ferrous Base.

Filter paper, saturated with solution containing 20 g.
sodium chloride, 1 g. potassium ferricyanide, 100 c.c.
water. Paper rinsed after test.

Fig. 64.

Gaslight paper, treated as described in Fig. 64.

Fig. 65.

Gaslight paper, treated as described in Fig. 64, but
lightly chilored, before test, with filter paper, and
not rinsed after test.

Fig. 66.

militate against sharp delineation (Fig. 65). Blurring of the impression is very frequently due to application of the paper in too damp a state ; it may also occur during subsequent washing.

Fig. 66 shows another impression obtained with the same paper and solution. In this case, however, before the paper was applied it was lightly dabbed with a filter paper and was not subsequently washed. This procedure prevents blurring of the impression, but there is some danger that the test paper may become too dry and that the indicator will consequently fail to react with some of the smaller pores.

Copper, Brass and Bronze Samples. The ferroxyl indicator may also be used for determination of porosity in coatings deposited on copper and copper alloys : the ferricyanide ion precipitates copper as a greenish-brown deposit. Apparently, however, the initial dissolu-
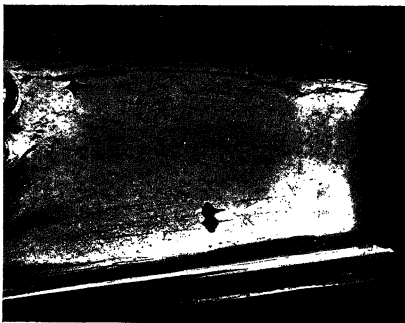
No. 49 : H
Copper-nickel-chromium Coating, on Brass.
Treated by pouring ferroxyl indicator solution over surface.
FIG. 67.

tion of the copper is accompanied by partial reduction of the ferricyanide ion to ferrocyanide ion and the ferrocyanide ion reacts with the cupric salts, giving a strongly marked rust-brown precipitate, $K_4[Fe(CN)_6] + 2CuCl_2 = 4KCl + Cu_2[Fe(CN)_6]$ known as Hatchett's brown. The red-brown precipitate contains aqueous cupric salts of ferrocyanic acid of varying alkali content.

Fig. 67 shows the impression of a sample from radiator shell H (brass base, coated with copper 2·5, nickel 4·5, chromium 0·5 μ), after treatment by pouring over a ferroxyl indicator solution (sodium chloride

1 g., agar-agar 2 g., potassium ferricyanide 0·1 g., water 100 c.c.). The photograph shows the very porous character of the plating, but does not differentiate between pores penetrating only through the chromium and nickel coatings to the copper underlay, and those extending to the brass base. It is, however, unusual to plate brass with copper prior to deposition of nickel and chromium.

Figs. 68 and 69 show the results obtained on the same specimens, using indicator papers saturated with a solution containing sodium chloride 10 g., potassium ferricyanide 1 g., water 100 c.c. These
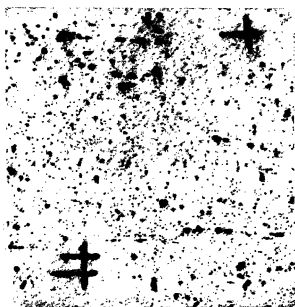
No. 49 : H.   Copper-nickel-chromium Coating, on Brass.
          Filter paper,   Gaslight paper,
both saturated with solution containing 10 g. sodium chloride, 1 g. potassium ferricyanide, 100 c.c. water.
          FIG. 68.   FIG. 69.

reproductions were free from the blurring effect found on the gelatin films from ferrous-base samples.

It has been stated that substitution of ammonium chloride for sodium chloride in the indicator solution gives a better definition of the pores. Pitschner [177] recommends the use of ammonium carbonate or ammonium citrate [see also 295].

Porosity tests of this type are sometimes unsuccessful due to the impossibility of bringing the copper ions into solution. The failure may be due to passivity of the brass, to the formation of protective films, or to the character of the galvanic links formed. To overcome this difficulty the Bureau of Standards recommends smearing the specimen with a pad soaked in dilute nitric acid, prior to application of the solution. Nitric acid, however, also attacks the nickel underlay and may therefore extend small pores through to the basis metal. The treatment is

obviously open to certain objections, though in certain cases it may be indispensable.

In view of the fact that when the ferroxyl indicator is used there is first a reduction of the ferri- to the ferro-cyanide ion, the Bureau of Standards recommends the substitution of potassium ferrocyanide for potassium ferricyanide in the indicator solution [331]. If a nitric acid solution is used, preliminary pickling of the work is unnecessary. The preferred composition of the indicator solution is given as potassium ferrocyanide 2g/l in 10 per cent. HNO_3 ; time of treatment 15 minutes. Potassium ferrocyanide is oxidised only slowly by nitric acid of this concentration, but it is advisable to add the ferrocyanide only just before the mixture is used.

E. Schürman and H. Blumenthal [180] use an indicator consisting of an ammoniacal solution of ammonium persulphate. This solution reacts with the cupric ions, forming a water-soluble cupric oxide-ammonium compound. The reaction, however, takes place without formation of a precipitate and with only slight colour effect : the indicator is therefore useless in determining porosity.

Strausser [537] states : " A method which yields fair results for nickel coatings on copper is to immerse the specimen in hydrogen sulphide water. Black spots appear where any appreciable area of copper is exposed, but fine pores are not readily detected."

The American Society for Steel Treating in its Data Sheet of Recommended Practice for Testing Metal Coatings on Bolts and Nuts [424], recommends testing of nickel plating on copper alloys by immersion in a solution containing trichloracetic acid 100 g., water 400 c.c., ammonium hydroxide (sp. gr. 0·90) 400 c.c. A blue coloration is produced at the sites of the pores.

The data summarised above indicate that the ferroxyl indicator is highly suitable for determination of porosity in coatings deposited on iron, copper or copper alloys. In the case of composite chromium coatings, in which an underlay of copper is embodied, this reagent permits of the simultaneous determination of the pores penetrating to the copper layer (brown coloration) and those extending to the ferrous base (blue coloration).

The very general use of nickel as underlay to chromium necessitates an indicator solution which will show the number of pores extending only as far as the nickel stratum. Dimethylglyoxime, added to the ferroxyl indicator solution, may be used for this purpose [315]. The dimethylglyoxime reacts with the nickel ions, giving the characteristic red precipitate[1]

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[1] Blum, Barrows and Brenner [331] report, however, that " it was not found possible to develop any reagent that will attack the nickel underlay and not

In order to bring the nickel ions into solution it is advisable to pickle with dilute nitric acid for a short time prior to application of the indicator solution. The chromium plating is not attacked by this treatment. If the indicator paper method is used, it is preferable to use gelatin paper: filter paper, due to unevenness of surface, fails to pick up and reproduce very small pores and cracks.

Aluminium- and Zinc-base Alloys [see also 295, 537]. Some difficulty was experienced in testing coatings deposited on aluminium alloy and zinc-base die castings, due to lack of any indicator which gives a strong coloration with the aluminium and zinc ions going into solution. Experiments were therefore made with indicators which would be reduced by the hydrogen evolved and would either become coloured or would lose their initial characteristic coloration. A section from J8 (nickel-chromium-plated aluminium alloy) was covered with a hot aqueous solution containing magnesium chloride 3 g., gelatin 10 g. per 100 c.c. ; a few drops of ferric chloride and potassium ferricyanide were added as indicators [228]. The hydrogen evolved reduces the ferric to ferrous ions and the ferrous ions react with the potassium ferricyanide, forming Turnbull blue. This treatment, however, produced an all-over blue coloration and failed to give the localised colour reaction required for determination of porosity. The use of the solution in a cold and slightly viscous condition results in a more localised reduction of the ferric ions, but the sensitivity of the reaction is reduced to such a degree that only very large pores are affected. Experiments with methylene blue, which is decolorised by reaction with hydrogen, showed that this reagent also is unsatisfactory for the purpose.

In the course of these experiments, however, it was observed that the hydrogen bubbles formed at the pores could be clearly detected, and an attempt was therefore made to utilise this observation for estimation of porosity. After careful degreasing, the specimens were covered with a highly viscous gelatin solution containing 2·5 per cent. sodium hydroxide. After a few minutes, hydrogen bubbles rose at all the pores extending through to the aluminium base, and remained fixed in the fluid gelatin at the points at which they first formed. The number of bubbles per sq. cm. of surface may be taken as a quantitative estimation of porosity. In order to prevent decomposition of the gelatin by the indicator solution, it is advisable to make the alkaline addition drop by drop, and to use a dilute solution, at a temperature of 25° C. (77° F.). (Fig. 70 shows the results of the test on J8.)

affect chromium. A solution containing 2 g/l of dimethylglyoxime in ammonium hydroxide (1–1) slowly produces a pink colour wherever nickel is exposed through chromium. As, however, the test requires 12–24 hours it is not suitable for inspection purposes.''

This method is not applicable for testing chromium plating deposited on zinc-base alloys or over an underlay of zinc, due to the fact that the solution is not sufficiently alkaline to cause hydrogen bubbles on zinc. On coated zinc materials pre-heated to 80° C., however, a solution of sugar, viscous when heated and containing about 30 per cent. sodium hydroxide, causes vigorous evolution of hydrogen at points at which the pores penetrate to the base. The solution solidifies on cooling and the hydrogen bubbles remain fixed for a period sufficiently long to

No. 65 : J 8
Nickel-chromium Coating, on Aluminium Alloy Casting.
Treated by pouring over the surface a 2·5% sodium hydroxide solution containing gelatin.
FIG. 70.

allow of making a count or taking a photograph of the film. The addition of about 5 per cent. of glycerine prevents crystallisation of the sugar.

In the case of metals so electro-negative as aluminium and zinc alloys, treatment in acid copper sulphate solution may also be used for detection of porosity [55].[1]

Since copper does not deposit readily on passive chromium, if a chromium-plated surface is used as cathode in an acid copper sulphate solution, copper will deposit only at positions where the underlay metal is exposed through pores or cracks in the chromium coating.

In experiments at the Bureau of Standards [331], it was found, however, that it is possible to deposit copper upon electrodeposited chromium, although a higher potential is needed than that required

    [1] This method is particularly recommended for chromium coatings applied direct to the base metal : in the presence of an underlay it is frequently impossible to differentiate between the pores and cracks extending through to the base and those penetrating only to the respective underlays.

to deposit copper on other metals. In order to ensure that the copper will deposit only on the exposed base metal and not on the chromium it is therefore necessary to control the applied voltage. It was found by the Bureau investigators that copper is deposited within 2 minutes, in sharply defined spots or lines, from a bath containing copper sulphate 200 g/1, sulphuric acid 75 g/1, when a potential of 0·1–0·2 volt is applied between a copper anode and a chromium-plated cathode about 5 cm. (2 inches) apart. The amount of copper deposited may be determined by weighing the sample before and after plating, or may be calculated by measurement of current density during deposition. Since effective cathode surface is represented by the amount of available basis material, with any given current density, anode surface and distance between the electrodes, the current density must stand in a definite ratio to the " cathode " surface, i.e. to the area of uncoated material exposed. The average current density (expressed in milliamps per sq. dm. of surface of work), measured over a period of 2 minutes, may, therefore, be taken as a measure of porosity. The amount of copper deposited must obviously depend to some extent on the depth of the pores and cracks, and it cannot be anticipated that exact quantitative values will be obtained : the results so calculated will, nevertheless, be a more reliable basis of comparison than those obtained by mere visual examination. (Fig. 71 shows J8 (aluminium alloy casting, nickel-chromium-plated) after light cathodic treatment in copper sulphate solution : Fig. 72 shows the deposition of copper at the pores.)

Due to the very high negative potential of zinc, it is possible to use the immersion process for testing chromium plating on zinc-base material. The specimens may be immersed for about 10 minutes in an aqueous sulphuric acid-copper sulphate solution (copper sulphate 10 g., conc. sulphuric acid 1 c.c., per 100 c.c. water). Due to its high solution pressure and its position in the electrochemical series, zinc goes into solution at the pores of the coating and a corresponding amount of copper is deposited.

Figs. 73, 74 and 75 show results of the immersion test on nickel- and nickel-chromium-plated zinc-base castings. In A1, the porosity is greatest at the corners of the handle on the underside and at the point at which it joins the shaft ; in A3 maximum porosity is on the underside of the handle. The copper at first deposits exclusively at the pores on the coating which penetrate to the zinc base, but since copper and nickel are close to one another in the electrochemical series, and nickel is at first even slightly less noble than copper (Table XIII) there is some risk that after the pores are closed, the copper may deposit on the nickel underlay. The treatment should be interrupted as soon as this stage is reached.

Fig. 76 shows J1 (copper 0·5, nickel 4·0, chromium 0·5 μ) and Fig. 77 a section from J9 (copper 0·4, nickel 2·5, chromium 0·6 μ), both after treatment by immersion in sulphuric acid-copper sulphate solution.

× 1

No. 65: J 8.   Nickel-chromium Coating on Aluminium Alloy Casting.
After light cathodic treatment in 1% copper sulphate solution containing sulphuric acid
(Dubpernell process).
FIG. 71.

× 40
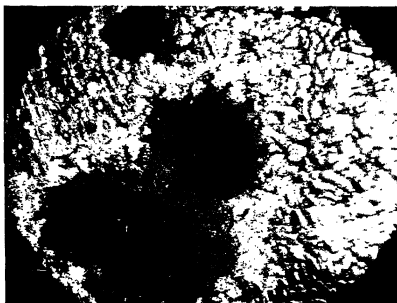
No. 65: J 8.   Nickel-chromium Coating on Aluminium Alloy Casting.
Showing precipitation of copper at the sites of the pores.
FIG. 72.

The former shows porosity and inadequate chromium-plating, especially between the wings : on the latter, pores and cracks are observed on the upper surface.
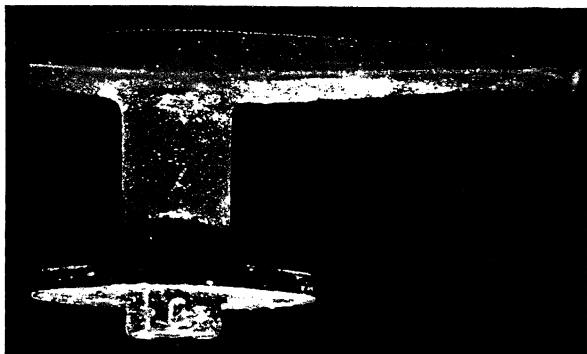
No. 58 : A 1
Nickel Coating on Zinc-base Die Casting.
After immersion in aqueous sulphuric acid--copper sulphate solution.
FIG. 73.
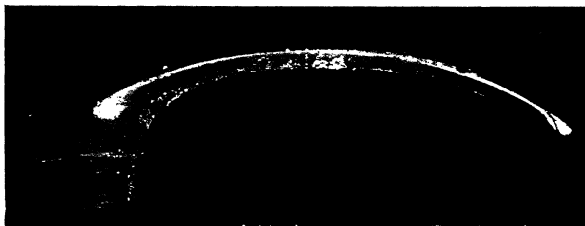
No. 59 : A 3
Nickel Coating on Zinc-base Die Casting.
After immersion in aqueous sulphuric acid--copper sulphate solution.
FIG. 74.

Porosity may also be tested by dissolving away the basis metal from the plating and determining the number and size of the pores by microscopical methods. Brook and Stott [237] used this method for examining porosity of coatings deposited on aluminium, employing sodium hydroxide as solvent for the aluminium. The method is obviously practicable only in cases where a reagent is available which
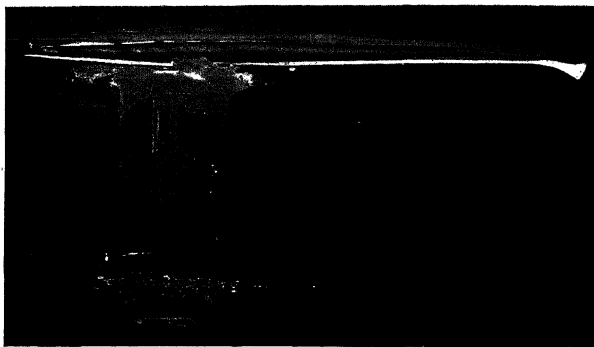
No. 60 : A 2
Nickel-chromium Coating on Zinc-base Die Casting.
After immersion in aqueous sulphuric acid–copper sulphate solution.

FIG. 75.

No. 61 : J 1
Copper-nickel-chromium Coating on Zinc-base Die Casting.
After immersion in aqueous sulphuric acid–copper sulphate solution.

FIG. 76.

× 1

No. 62 : J 9
Copper-nickel-chromium Coating on Zinc-base Die Casting.
After immersion in aqueous sulphuric acid–copper sulphate solution.
FIG. 77.

will attack the basis metal but not the metals of the interlay and surface coatings.

Porosity Tests on Automobile Components

As a result of the experiments described above, the following methods were selected for the porosity determinations on the automobile parts :

I. For ferrous-base samples the ferroxyl indicator method was employed, using a solution containing sodium chloride 20 g., potassium ferricyanide 1 g., water 100 c.c. The paper was left in contact with the surface of the specimens for five minutes.

II. For brass- or bronze-base samples the same method was used, but before treatment with the indicator, the specimens were pickled for a short time with dilute nitric acid. In the case of brass-base speci-mens it was not always possible to differentiate between pores extending through to the brass base and those penetrating only to the copper interlay.

III. Zinc-base samples were treated by two methods, viz. (a) immersion for 10 minutes in sulphuric acid-copper sulphate solution, (b) treatment with a hot sugar solution containing about 30 per cent. sodium hydroxide and 5 per cent. glycerine, the specimen being pre-heated to 80° C. (176° F.).

IV. Aluminium alloy samples were tested by pouring over a highly viscous gelatin solution containing 2·5 per cent. sodium hydroxide.

SUMMARY.

Table XVI shows the results of the porosity tests and Figs. 78–101 give some typical examples of the reproduction of the porous and

TABLE XVI.—POROSITY TESTS ON THE AUTOMOBILE COMPONENTS

Basis Metal	Exterior Coating	Component	Serial Number	Mark	Thickness of Intermediate Layers, μ.		Thickness of Exterior Coating, μ.		Fig.	No. of Pores per sq. cm.	Method used for Determ. of Porosity.
					Copper	Nickel	Nickel	Copper			
Iron or Steel	Nickel	Ornamental hub cap	1	C7	3·0	3·0	5·0	—	78	5	
	Chromium	Door handle	2	D2	—	—	—	0·3	79	4	
		Front-seat fitting	3	D3	—	—	—	0·4	—	9	
		Radiator shell	4	E1	0·4	1·5	—	0·5	80	14	
		Cable protection tube	5	J11	0·2	4·0	—	0·6	—	15	
		Gear handle	6	G11	0·2	7·0	—	0·6	—	12	
		Radiator shell	7	P1	0·2	8·0	—	0·7	81	4	
		Shock absorber housing	8	G19	0·5	13·0	—	0·5	—	18	I
		Lamp bracket	9	G4	0·4	16·0	—	0·8	82	1	
		Bonnet hinge	10	G18	0·5	22·0	—	0·6	—	1	
		Lamp bracket	11	C20	0·5	35·0	—	0·6	—	0·5	
		Bonnet screw	12	P4	0·3	37·0	—	0·4	—	0·1	
		Lamp cross-bar	13	N3	5·0	8·0	—	0·5	83	7	
		Lamp adjusting arm	14	G10	Brass 5·0	Nickel 5·0	—	0·5	84	12	
		Ventilating disc	15	K4	Zinc, Not determinable	Brass 5·5 / Nickel 3·0	—	0·4	86	90	
		Cap	16	K2		Brass 3·5 / Nickel 4·5	—	0·4	86	1	
		Wheel disc	17	K6		Brass 5·0 / Nickel 5·0	—	0·4	—	10	
		Beading	18	K10		Brass 4·0 / Nickel 8·0	—	0·4	—	9	
		Bumper	19	G6	Nickel 7·0	Copper 6·0 / Nickel 3·0	—	0·5	87	0·03	
		Bumper	20	M1	Nickel 7·0	Copper 35·0 / Nickel 2·0	—	0·75	—	0·06	
	Nickel	Exterior door handle	21	A4			3·0	—	88	28	
		Lamp fitting	22	C2			8·0	—	—	22	
		Running-board rail	23	C4	Nickel 2·5		—	—	89	5	
	Chromium	Door handle	24	D1		2·5	—	0·5	90	5	
		Radiator shell	25	G1		2·5	—	0·5	91	26	
		Badge	26	J5		2·5	—	0·5	91	18	
		Radiator screw cap	27	K11		2·5	—	0·4	—	15	
		Window adjuster	28	D4		3·5	—	1·0	—	11	
		Ornamental hub cap	29	E7		3·5	—	0·3	92	16	
		"Stop" lamp	30	G15		3·5	—	0·3	—		

116

Material	Coating	Part	No.	Code	Base metal (%)	Ni		0.x	Ref.		Class
Brass	Chromium	Cable protection tube	31	J11				0·5	98	11	II
		Hub cap	32	M2				0·6	94	7	
		Radiator shell	33	M3		3·5		0·4		21	
		Footboard plate	34	P2		4·0		0·4		19	
		Nut	35	G14		4·5		0·5		9	
		Cap	36	J4		4·5		0·5	95	10	
		Lamp casing	37	C3		5·0		0·5		14	
		Bonnet-support rail	38	C13		5·0		0·4	96	9	
		Radiator shell	39	N1		5·0		0·8		10	
		Hub cap	40	N2		5·0		0·5	97	9	
		Beading	41	K10		6·5		0·8		7	
		Bonnet stay	42	O9		8·0		0·7		4	
		Bonnet screw	43	K8		12·5		0·8		1	
		Lamp cap	44	O3		14·0					
		Bonnet-support rail	45	G8		25·0					
Bronze	Chromium	Knob	46	G13	Copper 0·5	Nickel 2·5		0·6		9	
		Ornamental hub cap	47	G5	Copper 0·5	Nickel 3·5		0·8		14	
		Radiator shell	48	P2	Copper 0·4	Nickel 4·0		0·7		14	
		Windscreen column	49	H	Copper 3·5	Nickel 4·5		0·4	93	36	
		Steering column	50	G17	Copper 0·3	Nickel 9·0		0·4	90	17	
		Bearing rod	51	J6	Copper 0·6			0·8	100	6	
		Rail	52	C5	Zinc 12·0		2·0	0·5	101	3	II
		Handle	53	B2			2·2	1·5	104	3	
		Steering-column bracket	54	B3				1·5		5	
		Roller bearing	55	B5				1·5	105	Not determd.	
		Steering-column bracket	56	B4				2·5		3	
		Lock	57	B1				3·5		1	
Zinc-base Die Castings	Nickel	Exterior door handle	58	A1					73	36	
		Interior door handle	59	A3					74	16	
	Chromium	Exterior door handle	60	A2	Nickel 2·0			0·3	75	8	
	Chromium	Radiator mascot	61	J1	Copper 0·5			0·5	76	10	III
		Radiator screw cap	62	J9	Copper 0·4			0·6	77	12	
		Radiator screw cap	63	B2	Brass 1·8			0·5		28	
Aluminium Alloy Castings	Chromium	Cover	64	J3	Nickel 3·0			0·5		Not determd.	IV
		Bracket	65	J8	Nickel 4·0			0·4	70	9	

unsound areas on the indicator films. The table and figures used in conjunction with one another provide a survey of (1) porosity of the individual samples, and (2) porosity as a function of thickness of coating. The ratings given below are the average numbers of pores per square centimetre of surface.

Porosity Tests on Automobile Components

Ferrous Samples. Rating 0·03–20 pores per sq. cm. (Table XVI : Figs. 78–87).

In examining Figs. 78–87 it must be remembered that the ferroxyl indicator reveals both the pores extending through to the base (blue coloration) and those penetrating only to the copper interlay (red coloration). In assessing porosity only the former type were counted. The photographic method of reproduction, which does not permit of differentiation between the two types, introduces especially large discrepancies in the case of samples having a thick underlay of copper.

Due to the limited amount of material available, no definite conclusions can be drawn regarding the influence of the underlay metal(s). K6 and K10 (brass-nickel-chromium-plated) in spite of a thickness of 4·5–5 μ brass, show a high porosity rating (9·20), whereas K2 (brass 3·5, nickel 4·5, chromium 0·4 μ) is only slightly porous (rating 1). G6 and M1 (nickel-copper-nickel-chromium) gave the lowest porosity count (0·03–0·06). In view of the fact that the *total thickness* of coating on these samples (47 and 45 μ respectively) is in excess of that on any other specimens examined, it is possible that the superior properties may be primarily attributable to additional *total* thickness. This isolated example does not, however, justify a final conclusion as to the peculiar efficacy of the particular type of coating. F4 (copper-nickel-chromium-plated), which comes next to G6 and M1 in respect of total thickness of coating (37 μ), also shows a very low porosity rating (0·1).

The larger number of copper-nickel-chromium-plated samples available (Table XVI, Nos. 4–13) permits of some assessment of the influence of thickness of coating on porosity. The copper underlay varied from 0·2 to 0·5 μ, and the chromium from 0·4 to 0·8 μ : the nickel ranged from 1·5 to 37 μ. Fig. 102 (porosity as a function of thickness of nickel underlay) shows that with increasing thickness of nickel, the soundness and density of the plating rises very rapidly, the improvement in properties being more than proportional to the increase in thickness of nickel. At a thickness of 40 μ the porosity value falls to zero.

It is well known that porosity is affected to an important extent by conditions of deposition, but these curves indicate that *thickness* of

No. 1 : C 7
Copper-nickel Coating, on Ferrous Base.
5 pores per sq. cm.
FIG. 78.

No. 3 : D 3
Nickel-chromium Coating, on Ferrous Base.
9 pores per sq. cm.
FIG. 79.

× 1
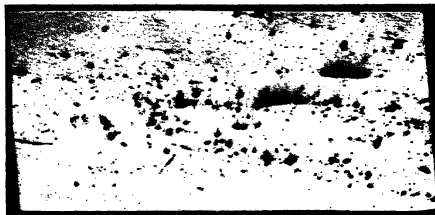
No. 5 : J 11
Copper-nickel-chromium Coating, on Ferrous Base.
15 pores per sq. cm.
FIG. 80.
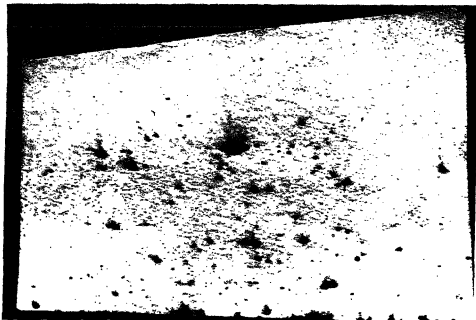
No. 7 : F 1
Copper-nickel-chromium Coating, on Ferrous Base.
4 pores per sq. cm.
FIG. 81.

No. 9 : G 4
Copper-nickel-chromium Coating, on Ferrous Base.
1 pore per sq. cm.
FIG. 82.

× 1

No. 13 : N 3
Copper-nickel-chromium Coating, on Ferrous Base.
7 pores per sq. cm.
FIG. 83.

No. 14 : G 10
Brass-nickel-chromium
Coating, on Ferrous
Base.
12 pores per sq. cm.

FIG. 84.
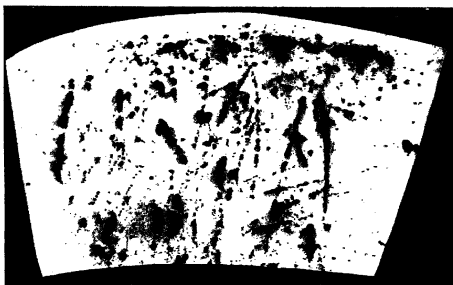
No. 15 : K 4
Zinc-brass-nickel-chromium Coating, on Ferrous Base.
20 pores per sq. cm.
FIG. 85.
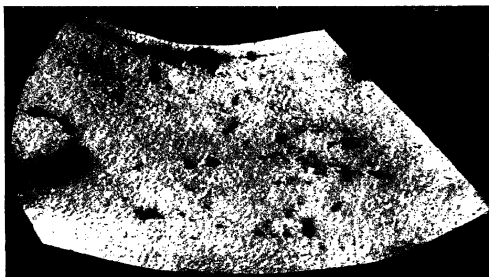
No. 17 : K 6
Zinc-brass-nickel-chromium Coating, on Ferrous Base.
10 pores per sq. cm.
FIG. 86.

plating is also a strongly determining factor. The results confirm (1) the findings of previous authors that nickel plating 25–30 μ thick may be considered practically free from porosity [278] and (2) the results obtained by the Bureau of Standards [134] according to which the

× 1

No. 19 : G 6
Nickel-copper-nickel-chromium Coating, on Ferrous Base.
0·03 pores per sq. cm.
FIG. 87.

increase in the protective value of the plating is more than proportional to the increase in thickness. (See also Blum, Barrows and Brenner [331], who found that " under customary conditions of plating, e.g., at 45° C., chromium deposits on steel showed the greatest porosity, those on nickel the least.")

Brass Samples. Rating 1–36 pores per sq. cm. (Table XVI, Figs. 88–101).

With only a few exceptions, all the samples were nickel-chromium-plated. The nickel-plated samples A4 and C2 show a high rating (22–28), but in specimens carrying a nickel layer of equal thickness plus a surface coating of chromium the average porosity is considerably lower. C4 (3 μ chromium without underlay) and C5 (zinc-chromium-plated) were only slightly porous.

A few specimens carried a thin layer of copper under the nickel, and on one sample (H) the copper plating was 2·5 μ thick. The possible effect on porosity of the additional copper interlay cannot be established, since the ferroxyl indicator reacts in a similar manner with both the brass and the copper, and the tests therefore do not indicate the proportion of the pores extending through to the basis metal.

Fig. 103 shows porosity of the nickel-chromium-plated brass-base samples (24–45) as a function of thickness of nickel underlay. The chromium coating on these samples varied from 0·3 to 1 μ; the nickel underlays were 2·5 to 25 μ. The curve obtained is similar

No. 22 : C 2

Nickel Coating, on Brass.

22 pores per sq. cm.

FIG. 88.

No. 23 : C 4

Chromium Coating, on Brass.

5 pores per sq. cm.

FIG. 89.

× 1
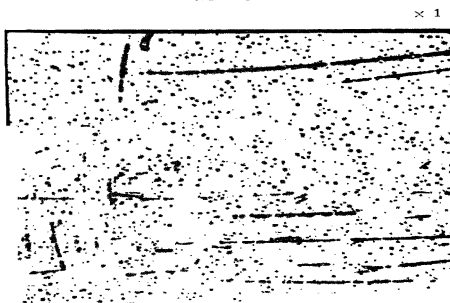
No. 25 : G 1

Nickel-chromium Coating, on Brass.

26 pores per sq. cm.

FIG. 90.

× 1

No. 27 : K 11
Nickel-chromium Coating, on Brass.
15 pores per sq. cm.
FIG. 91.

× 1

No. 30 : G 15

Nickel-chromium Coating,
on Brass.

16 pores per sq. cm.

FIG. 92.
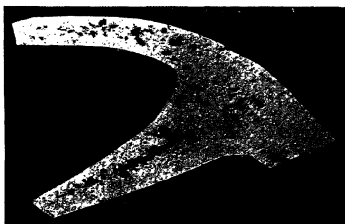
× 1
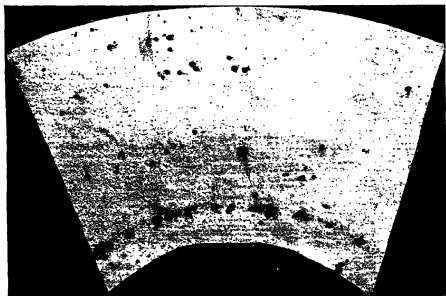
No. 32 : M 2
Nickel-chromium Coating, on Brass.
7 pores per sq. cm.
FIG. 93.

× 1

No. 33 : M 3
Nickel-chromium Coating, on Brass.
21 pores per sq. cm.

Fig. 94.

× 1

No. 38 : C 13
Nickel-chromium Coating, on Brass.
9 pores per sq. cm.

Fig. 95.

× 1
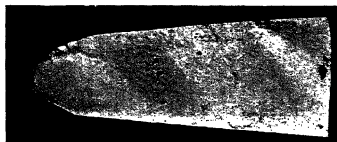
No. 42 : G 9
Nickel-chromium Coating, on Brass.
3 pores per sq. cm.

Fig. 96.
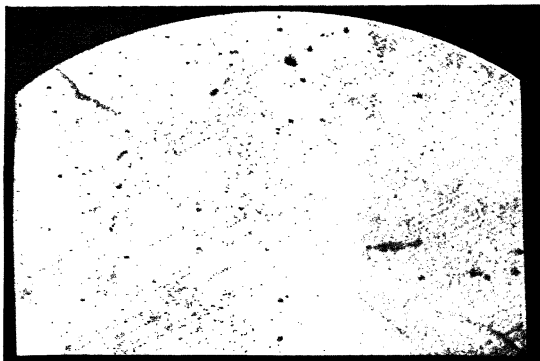
No. 44 : G 3
Nickel-chromium Coating, on Brass.
1 pore per sq. cm.
FIG. 97.
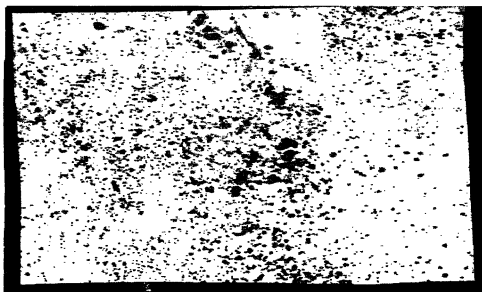
No. 49 : H
Copper-nickel-chromium Coating, on Brass.
36 pores per sq. cm.
FIG. 98.

No. 50 : G 17
Copper-nickel-chromium Coating, on Brass.
17 pores per sq. cm.

FIG. 99.
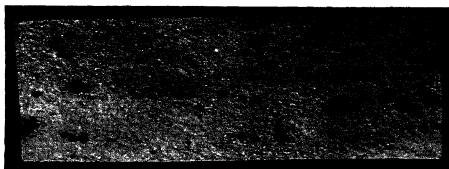
No. 51 : J 6
Copper-nickel-chromium Coating, on Brass.
6 pores per sq. cm.

FIG. 100.

No. 52 : C 5
Zinc-chromium Coating, on Brass.
3 pores per sq. cm.

FIG. 101.

127

in character to that given by the copper-nickel-chromium-plated ferrous-base samples, and fully confirms the conclusions drawn from Fig. 102.

The wide variation in the porosity count of thin coatings is very noteworthy. For example, D1, with a 2·5 μ nickel underlay, has a rating of only 5, whereas G1, with a coating of equal thickness, shows 26 pores per sq. cm. The data indicate that freedom from porosity may be obtained even in thin coatings, provided that correct conditions of deposition are ensured. These conditions apparently require to be
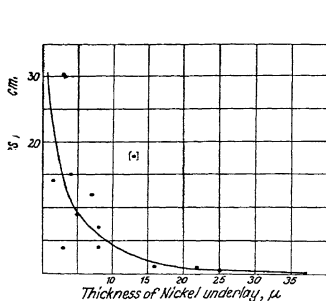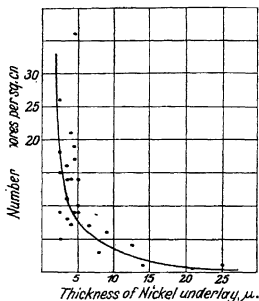
Ferrous Samples.   Brass Samples.

Porosity of Automobile Samples.
Influence of Thickness of Nickel Underlay.

FIG. 102.   FIG. 103.

controlled within very narrow limits, and even slight deviation results in severe increase in porosity. In the case of the heavier coatings, the porosity varies within a considerably narrower range, and the effect of additional thickness masks that of the conditions of deposition.

Bronze Samples. Rating 1·5 pores per sq. cm. (Table XVI, Figs. 104, 105).

The few samples submitted were plated with a relatively thick coating of chromium (1·5–3 μ), deposited without underlay. In view of the paucity of the material available, no comparisons of different types of coating were possible, and the small number of samples of the one type rendered impossible any correlation of porosity with thickness of coating.

No. 54 : B 3
Chromium Coating, on Bronze.
5 pores per sq. cm.

Fig. 104.

× 1

No. 57 : B 1
Chromium Coating, on Bronze.
1 pore per sq. cm.

Fig. 105.

Zinc-base Die Castings. Rating 8–36 pores per sq. cm. (Table XVI).

The nickel-chromium-plated samples A1 and A3, carrying, respectively, 2·0 and 2·2 μ of nickel, had ratings of 36 and 16, the underlay of nickel being too thin to ensure soundness even with a superimposed coating of chromium. The best results in this group were given by A2 (nickel-chromium-plated) which had a rating of 8.

Aluminium Alloy Castings. Rating 8 pores per sq. cm. (Table XVI).

Only one porosity test was made, on the nickel-chromium-coated sample J8. This specimen showed a moderately good rating (8), but some of the pores were of considerable depth and size.

CORROSION TESTS

Methods of Test

The methods of test used were selected as representative of conditions encountered in service : determination of the behaviour of the coatings under atmospheric exposure (weathering tests) was considered to be of primary importance. In view of the fact that a leading automobile works had reported bad behaviour of chromium plating in the coastal area of the North Sea, the test conditions were extended to include exposure to sea-water attack. Laboratory salt-water spray tests were also included in the programme.

Metal coatings on automobile parts are also subject to corrosive attack by polishing media, fuels, cleaning compositions and any other materials which come into contact with the plating in the course of driving or upkeep. A series of corrosion tests was therefore made, using such substances as the attacking media.

Atmospheric exposure tests have the disadvantage that the results are affected by the period of the year at which the tests are made, and by the weather and climatic conditions operative during any one series of tests (see 485). The results of such tests cannot, therefore, be considered absolute, but must be used as a basis of comparison only.

The reagent most generally used for spray tests is the 3 per cent. sodium chloride solution, as standardised for the testing of aluminium and aluminium alloys : a 20 per cent. concentration is also used [470, 537, 548].[1] In America a 20 per cent. calcium chloride solution is sometimes employed [300, 316], to simulate the water used for spraying the streets. Thompson and Jelen [470] used ammonium sulphate for testing chromium plating on zinc. Solutions of N/100 sulphuric acid and a solution containing ammonium sulphate (16 g./litre) with ammonium chloride (4 g./litre) have also been used, to simulate,

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[1] See also French work dealing with (1) composition of artificial sea water for corrosion tests and (2) standardisation of sodium chloride tests [514, 532]: also general discussion of accelerated test conditions [178, 205, 261]. A 20 per cent. solution is recommended by the American Society for Testing Materials, see also pp. 42, 154 and 221.

respectively, rain falling over industrial districts, and atmospheres containing ammonium sulphate. Bannister [482] gives a useful summary of spray test methods.

In view of the poor agreement sometimes found between the results of atmospheric exposure and spray tests it is impossible strictly to compare data obtained by the two methods [134, 183, 458]. The D.V.L., for example, in testing light metals, obtained good agreement between the two sets of tests [260],[1] whereas Mougey [300] testing chromium plating, reported discrepancies between the results obtained by atmospheric exposure and the ratings by the sodium chloride or calcium chloride spray.

Chromium is distinguished among the metals by its very high chemical stability ; it is especially resistant to compounds found in the atmosphere, carbon dioxide, ammonia, nitric acid, rain water, sea water, sulphur dioxide [121, 131, 152, 221, 485, 521].

Nickel when exposed to the air, after a time becomes coated with a thin film of corrosion product which tends to protect the metal from further attack [202, 245, 419].

If, therefore, chromium or nickel coatings absolutely free from porosity could be produced, no corrosion attack would take place under the conditions to which nickel- or chromium-plating is subject in automobile service. In view of the porosity of commercial coatings, however, the electrochemical relationship of the basis and underlay metals is a factor of very considerable importance (see preceding chapter).

Corrosion of nickel- or chromium-plated parts is usually characterised by one or more of the following effects :

1. Formation of nodules of corrosion product, originating at the pores on the exterior coating.

2. Localised flaking or peeling of the coating.

3. Removal of the whole coating.

The varied effect of corrosion attack, the multifarious forms of component, the differences in the basis metals used, the extreme thinness of the coatings, and other variables very severely limit the utility of certain forms of corrosion test, as, for example, determinations of loss in weight or of change in mechanical properties or structure due to corrosion. Observation of change in surface condition is the only practicable method of assessing behaviour under corrosive attack, and if accurate and consistent comparison is to be made on this basis, standards must be formulated for assessment of the appearance of the plating.[2]

---

[1] This paper contains a report of extensive study of accelerated test methods, carried out under the ægis of the Deutsches Verein für Luftfahrt.

[2] A method of rating standardised for the A.E.S.—A.S.T.M.—N.B.S. tests is based on percentage calculation of rusted/unrusted surface, multiplied by the number of weeks required for attainment of a given degree of corrosion [485].

In the tests reported below, three grades of attack were standardised, viz. :

" slight corrosion " (α) = tarnishing of the surface or slight local
attack.

" moderate corrosion " (β) = small patches of corrosion, staining
and blistering, *without* visible deterioration of the coating after
removal of the corrosion product.

" severe corrosion " (γ) = disintegration of the coating, or partial
decomposition remaining visible after removal of the corrosion products.

The rating assigned (G), is the number of weeks required for onset
of " severe " corrosion (γ). Fig. 106 shows the standard samples.
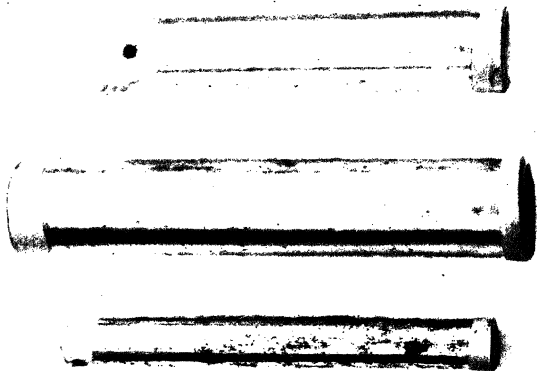
Fig. 106.—Standard Samples for Assessment of Corrosion Resistance.
(Copper-nickel-chromium coatings, on Steel.)

α, " slight corrosion " = slight localised patches of rust.
β, " moderate corrosion " = numerous evenly distributed slight patches of rust ; coating remaining intact.
γ, " severe corrosion " = numerous heavy patches of rust ; coating partially disintegrated.

Atmospheric Tests (Weathering Tests) (see Table XVII)

Samples selected for test were of even and flat surface and were in
comparable surface condition. Test pieces 100 × 50 mm. (4 × 2
inches) were taken from large components : smaller parts were tested
whole. All test pieces were degreased with ether and alcohol before
testing.

The specimens were fastened by string to a wooden frame in

clined at 45° facing South (see Fig. 107) : cut edges were protected with paraffin wax. The specimens were inspected at fixed intervals and observations were made on surface condition.

Ferrous Samples. Table XVII shows the degree of attack after one, six and twelve months respectively ; where necessary, the standard designations, α, β, γ, are supplemented by photographs.[1]

In general, the nickel- and chromium-plated ferrous-base samples

FIG. 107.—Atmospheric Exposure Tests.
Arrangement of Specimens.

showed poor resistance to corrosion. The attack originated, in all cases, at the pores on the surface coating, the first indication being the formation of small localised patches of rust, which, in the case of very porous and thin coatings, rapidly spread and formed a continuous film of rust. In less porous coatings the localised corrosion patches spread more gradually, resulting ultimately in scaling and peeling of the coating. The areas of the chromium plating which remained free from rust

[1] The photographs give a somewhat inadequate impression of the change in surface condition ; in some cases the effect is minimised, in others exaggerated.

TABLE XVII.—Atmospheric Exposure (Weathering) Tests on the Automobile Components

Basis Metal	Exterior Coating	Component	Serial Number	Mark	Thickness of Intermediate Layers, μ. Copper	Nickel	Thickness of Exterior Coating, μ. Nickel	Chromium	Condition of Surface after 1 mth.	Fig.	6 mths.	Fig.	12 mths.	Fig.	Fig. of Merit (Number of Works to produce γ-type Corrosion)
Iron or Steel	Nickel	Ornamental hub cap	1	C7	3·0	3·0	5·0		β	108	γ	109	γ		6
		Door handle	2	P2		3·0		0·3	γ	110	γ		γ		2 2 2 1
		Front-seat fitting	3	D3		3·0		0·4	γ		γ		γ		2 2 2 1
	Chromium	Radiator shell	4	R1	0·4	1·5		0·4	γ	111	γ		γ		4
		Cable protection tube	5	J11	0·2	4·5		0·5	γ		γ		γ		11
		Rear handle	6	G11	0·3	7·0		0·6	γ		γ		γ		16
		Radiator shell	7	F1	0·2	8·0		0·7	γ		γ		γ		18
		Shock-absorber housing	8	G10	0·5	13·0		0·5	α	100B	γ	112	γ		16
		Lamp bracket	9	G4	0·4	16·0		0·8	α		γ		γ		18
		Bonnet hinge	10	G18	0·5	22·0		0·5	α		γ		γ		16
		Lamp bracket	11	C20	0·5	25·0		0·6	α		γ		γ		16
		Bonnet screw	12	P4	0·3	37·4		0·5	γ		γ		γ		16
		Lamp crossbar	13	N3	5·0	8·0		0·5	γ		γ		γ		16
		Lamp adjusting arm	14	G10	Brass 5·0	5·0	5·0		γ	113	γ		γ		3
		Ventilating disc	15	K4	Zinc not determinable	Brass 5·5	3·0	0·4	γ		γ		γ		2 2 2 3
		Cap	16	K2		3·5	4·5		γ		γ		γ		2 2 2 3
		Wheel disc	17	K6		4·0	5·0		γ		γ		γ		
		Beading	18	K10		8·0	8·0		γ		γ		γ		
		Bumper	19	G8	Nickel 6·0	Copper 7·0		0·5	α	114	α		α	115	> 32
		Bumper	20	M1	7·0	35·0		0·75	α		α		γ		39
	Nickel	Exterior door handle	21	A4			3·0		β		β		β		52
		Lamp fitting	22	C2			8·0		β		β		β		39
		Running-board rail	23	C4		Nickel 5·0	3·0		β	118	β	119	γ		46
		Door handle	24	D1		2·5	0·5		β	120	β		β	121	32
		Radiator shell	25	G1		2·5	0·5		γ		γ		β		32
		Badge	26	J5		2·5	0·5		β		γ		γ		12
		Radiator screw cap	27	K11		2·5	1·0		β		β		β		22
		Window adjuster	28	D4		3·5	0·3		γ		γ		β		32
		Ornamental hub cap	29	E7		3·5	0·5		β		β		β		32
		"Stop" lamp	30	G15		3·5			β		β		β		32

Brass	Chromium	Cable protection tube	31	J11	3·5		—	0·5	α 1 mth.	—	β	122	β	—	> 52
		Hub cap	32	M2	4·0		—	0·5	α	—	α	—	α	—	> 52
		Radiator shell . .	33	M3	4·0		—	0·4	α	—	α	—	α	—	> 52
		Footboard plate .	34	F3	4·5		—	0·4	α	—	β	—	γ	123	46
		Nut	35	G14	4·5		—	0·5	α	—	α	—	α	—	> 52
		Cap	36	J4	5·0		—	0·5	α	—	α	—	α	—	> 52
		Lamp casing . .	37	C3	5·0		—	0·5	α	—	α	—	α	—	> 52
		Bonnet-support rail	38	C13	5·0		—	0·5	α	—	α	—	α	—	> 52
		Radiator shell . .	39	N1	5·0		—	0·5	α	—	α	—	γ	—	46
		Hub cap	40	N2	5·0		—	0·5	α	—	β	—	β	—	> 52
		Beading	41	K10	6·5		—	0·4	α	—	α	—	α	—	> 52
		Bonnet stay . .	42	G9	8·0		—	0·8	α	—	α	—	α	—	> 52
		Bonnet screw . .	43	K8	12·5		—	0·5	α	—	β	—	β	—	> 52
		Lamp cap . . .	44	G3	14·0		—	0·7	α	—	α	—	α	—	> 52
		Bonnet-support rail	45	G8	25·0		—	0·8	α	—	α	—	α	—	> 52
					Copper	Nickel									
		Knob	46	G13	0·5	2·5	—	0·6	α	—	α	—	α	—	> 52
		Ornamental hub cap	47	G5	0·5	3·5	—	0·8	α	—	α	—	α	—	> 52
		" " "	48	F2	0·4	4·0	—	0·7	α	—	α	—	α	—	> 52
		Radiator shell . " .	49	H	2·5	4·5	—	0·5	α	—	α	—	α	—	> 52
		Windscreen column	50	G17	0·3	4·5	—	0·6	α	—	β	—	β	—	> 52
		Bracing rod . . .	51	J6	0·6	9·0	—	0·8	α	—	α	—	α	—	> 52
					Zinc										
		Rail	52	C5	120		—	0·5	β	—	β	—	γ	—	39
Bronze	Chromium	Handle	53	B2	—		—	1·5	α	—	α	—	β	—	> 52
		Steering-column bracket . . .	54	B3	—		—	1·5	α	—	γ	—	γ	—	22
		Roller bearing . .	55	B5	—		—	1·5	α	—	γ	—	γ	—	23
		Steering-column bracket . . .	56	B4	—		—	2·5	α	—	α	—	β	—	> 52
		Lock	57	B1	—		—	3·5	α	—	γ	—	γ	—	24
Zinc-base Die Castings	Nickel	Exterior door handle	58	A1	—		2·0	—	2 weeks. β	124	γ	—	Test discontinued, peeling having occurred after 10–15 weeks' exposure. (γ).		15
		Interior door handle	59	A3	—		2·2	—	β	—	γ	—			15
	Chromium				Nickel										
		Exterior door handle	60	A2	2·0		—	0·3	β	125	γ	—			10
					Copper	Nickel									
		Radiator mascot .	61	J1	0·5	4·0	—	0·5	β	—	γ	—			10
		Radiator screw cap	62	J9	0·4	2·5	—	0·6	β	126	γ	127			10
					Brass	Nickel									
		Radiator screw cap .	63	E2	0·3	1·8	—	0·5	β	—	γ	—			10
Aluminium Alloy Castings	Chromium				Nickel										
		Cover	64	J3	3·0		—	0·5	β	128	γ	129			10
		Bracket	65	J8	4·0		—	0·4	β	—	γ	—			10

No. 1 : C 7
Atmospheric Exposure Test.
Copper-nickel Coating, on Ferrous Base.
γ-type corrosion after 6 months.
FIG. 109.

patches preserved their lustre, while the corresponding areas on the nickel plating became covered with a yellow-green film. The one nickel-plated sample (No. 1 : C7) was "moderately" corroded after only one month (β) ; after

× 1

six weeks, incipient flaking of the plating was observed (G = 6). Figs. 108 and 109 show this specimen after one month and after six months respectively.

Of the nineteen chromium-plated ferrous-base specimens, eleven showed incipient flaking and peeling (γ) after two to four weeks. Figs. 110, 111 and 113 are typical examples.

No. 9 (G4) was used as the standard sample (Fig. 106β). After sixteen weeks this specimen also showed incipient peeling, see Fig. 112 (G = 16).

No. 19 (G6) showed outstandingly good behaviour (Fig. 114) :

× 1

Atmospheric Exposure Test.
No. 3 : D 3
Nickel-chromium Coating, on Ferrous
Base.
γ-type corrosion after 1 month.
FIG. 110.
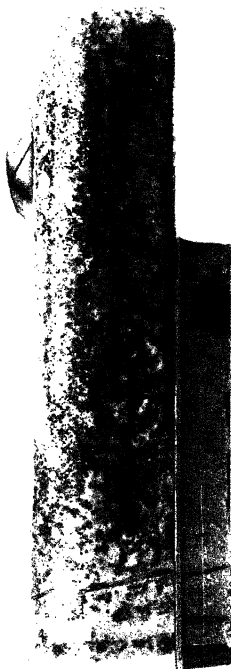
Atmospheric Exposure Test.
No. 4 : E 1
Copper-nickel-chromium Coating, on
Ferrous Base.
γ type corrosion after 1 month.
FIG. 111.

× 1

Atmospheric Exposure Test.
No. 9 : G 4
Copper-nickel Coating, on Ferrous
Base.
γ-type corrosion after 6 months.
FIG. 112.
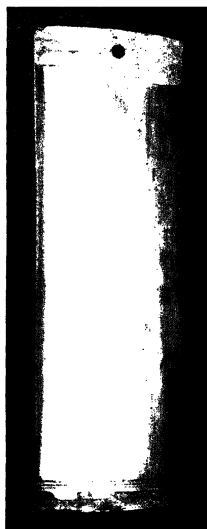
Atmospheric Exposure Test.
No. 19 : G 6
Nickel-copper-nickel-chromium Coat-
ing, on Ferrous Base.
α-type corrosion after 6 months.
FIG. 114.

Atmospheric Exposure Test.
No. 15 : K 4
Zinc-brass-nickel-chromium
Coating, on Ferrous Base.
γ-type corrosion after 1 month.
FIG. 113.
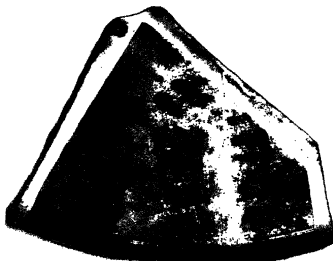
after twelve months only " slight " (α) attack was observed (G $=$ $>$52).
It should be noted that this sample had a very thick underlay of nickel
(7 $+$ 33 μ). The rating of No. 20 (M1), which had a copper underlay
of 35 μ, was high in comparison with other chromium-plated ferrous
specimens, but not equal to No. 19, since after thirty-nine weeks

$\times$ 1
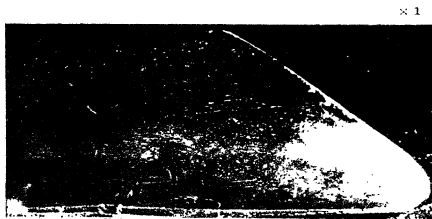
Atmospheric Exposure Test.
No. 20 : M 1
Nickel-copper-nickel-chromium Coating, on Ferrous Base.
γ-type corrosion after 12 months.
FIG. 115.

the nickel underlay, as well as the chromium coating, had flaked off,
leaving the copper underlay exposed.[1] In this sample the nodules
which appeared at the surface pores were not rusty-brown, as in the
case of all the other specimens, but greenish-brown patches of copper
salts, which gradually spread and finally covered the whole surface.
The film could easily be wiped off. Fig. 115 shows the specimen after
removal of the film ; the scaling of the coating is still visible.

The results indicate that the degree of protection afforded by metal
coatings depends on : (1) the soundness of the coating (its freedom from
porosity) and (2) the thickness of the intermediate layers, in particular
of the nickel underlay.

Fig. 116 shows the ratings (G) of the nickel-chromium-plated ferrous
specimens as a function of porosity rating. With only one pore per
sq. cm., the figure of merit falls rapidly ; at 4 it is quite low ; from
9 to 20 it remains practically constant. It is obvious that in chromium
plating on a ferrous base even slight porosity is sufficient to cause rapid
flaking or peeling of the coating.

Fig. 117 shows the behaviour of the same group of specimens as a
function of thickness of nickel underlay. With increasing thickness of

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[1] In connection with the relative value of copper and nickel underlays, see
pp. 193 and 221.

nickel the figure of merit rises rapidly, confirming the primary importance of a heavy nickel underlay.
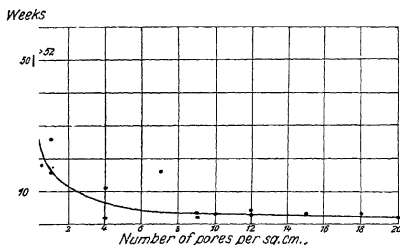
FIG. 116.—Atmospheric Exposure Test.   Life of Nickel-chromium-coated Ferrous-base Samples as a Function of Porosity Rating.
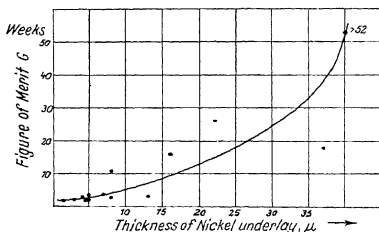
FIG. 117.—Atmospheric Exposure Test.   Life of Nickel-chromium-coated Ferrous-base Samples as a Function of Thickness of Nickel Underlay.

Brass Samples.   Generally speaking, the brass-base samples showed much more satisfactory resistance to atmospheric corrosion than the ferrous-base specimens: more than three months' exposure was required to produce even α-type attack. Corrosion took the form of spotty excrescences of a brownish-violet colour, which grew into patches of discoloration and finally covered the whole surface with a thin film. This film could easily be removed by polishing and after this treatment the surface of the plating showed no signs of deterioration. Similar effects were observed by Phillips in the St. Louis district [362]. Phillips also observed that copper and brass specimens on which the chromium was plated direct, or over an inadequate thickness of nickel, developed matt areas and showed a yellow-brown discoloration. Chem-

ical examination of the affected regions showed that the corrosion product on the chromium-plated brass specimen contained zinc and copper salts, while in the case of chromium-plated copper, the deposit consisted of copper salts. The chromium itself had remained unattacked. but the corrosive attack had resulted in the formation of a layer of the salts or oxides of the basis or interlay metals.

Some few of the specimens remained intact for a period of twelve weeks or longer. Of the thirty-two brass-base specimens examined, six did not show the γ form of attack until twelve months had elapsed.

The nickel-plated sample No. 22, after three months' exposure, showed a thin brownish-violet film which could easily be wiped off, leaving the surface clean and bright (α). After twelve months the coating was beginning to peel off (γ).

Sample No. 23 (C4), chromium-plated without underlay, after only one month's exposure showed the spots and excrescences typical of the β-type of attack (Fig. 118); after six months its condition had undergone no further material change (Fig. 119) but after forty-six weeks incipient peeling was observed.

Contrary to anticipation, No. 27 (K11), chromium-plated over a nickel underlay, showed the worst behaviour (Figs. 120 and 121): the nature of the corrosion, however, indicates that the rapid deterioration was due rather to poor adhesion than to porosity.

Fig. 122 shows β-type corrosion after six months in No. 31 (J11); Fig. 123 illustrates the incipient flaking in No. 34 (F3).

The copper-nickel-chromium-plated samples, Nos. 46–51, behaved particularly well. Nos. 46–49 and No. 51 showed α-type corrosion only, and had a figure of merit of > 52. In the zinc-chromium-plated sample No. 52 (C5) the chromium plating flaked off after thirty-nine weeks' exposure (G = 39).[1]

Bronze Samples. The behaviour of this group was similar to that of the brass-base samples. Brownish-violet patches first formed at the pores and gradually spread in a thin film over the entire surface ; in most cases the deposit could also at this stage easily be wiped off (α-type corrosion). After exposure for twenty-two to twenty-four weeks, however, scaling of the chromium plating (γ-type attack) was observed in three of the five samples tested.

The percentage of bronze-base samples showing γ-type corrosion is therefore considerably higher than the brass specimens chromium-plated over an underlay of nickel. Since none of the bronze-base specimens submitted had an underlay of nickel, it was impossible to determine whether this factor was responsible for their inferior corrosion resistance (see, however, later conclusions. pp. 160–1 and 211).

× 1

Atmospheric Exposure Test.
No. 23 : C 4
Chromium Coating, on Brass.
β-type corrosion after 3 months.
FIG. 118.

× 1

Atmospheric Exposure Test.
No. 23 : C 4
Chromium Coating, on Brass.
β-type corrosion after 6 months.
FIG. 119.

× 1
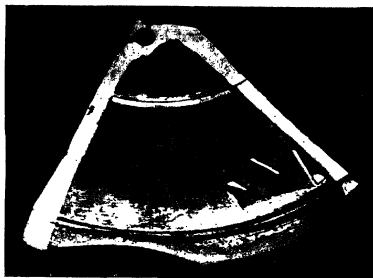
Atmospheric Exposure Test.
No. 27 : K 11
Nickel-chromium Coating, on Brass.
γ-type corrosion after 3 months, showing peeling of the coating.
FIG. 120.

× 1

Atmospheric Exposure Test.

No. 27 : K 11

Nickel-chromium Coating, on Brass.

γ-type corrosion after 6 months, showing severe peeling of the coating.

FIG. 121.

× 1
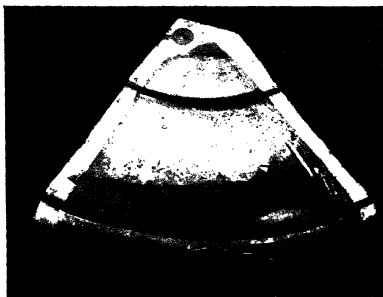
Atmospheric Exposure Test.
No. 31 : J 11
Chromium Coating, on Brass.
β-type corrosion after 6 months.
FIG. 122.

× 1
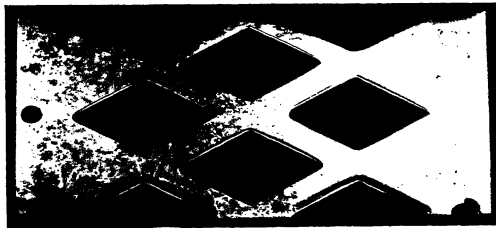
Atmospheric Exposure Test.
No. 34 : F 3
Nickel-chromium Coating, on Brass.
γ-type corrosion after 12 months, showing peeling of the coating.
FIG. 123.

143

Zinc-base Die Castings. The nickel and chromium coatings on
the zinc-base specimens afforded but little protection against atmo-
spheric attack. After only one week's exposure white patches appeared,
giving the specimens a spotty appearance,[1] the local corrosion gradually

× 1
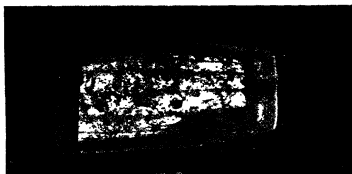
Atmospheric Exposure Test.
No. 58 : A 1
Nickel-chromium Coating, on Zinc-base Die Casting.
β-type corrosion after 2 weeks.
Fig. 124.

× 1

Atmospheric Exposure Test.
No. 60 : A 2
Nickel-chromium Coating, on Zinc-base Die Casting.
β-type corrosion after 2 weeks.
Fig. 125.

spread and after ten to fifteen weeks the plating flaked off. Figs. 124,
125 and 126 show the condition of Nos. 58, 60 and 62 after two weeks'
exposure. The patches of corrosion cover almost the entire surface
of the specimens. Fig. 127 shows No. 62 after six months.

Aluminium Alloy Castings. The chromium-plated aluminium
alloy specimens also behaved unsatisfactorily. The corrosion product
was of a yellow-white colour, and after ten weeks, flaking and peeling
of the coating was observed. Fig. 128 shows No. 64 after two weeks'
exposure, and Fig. 129 the same specimen after six months, after removal
of the thick layer of corrosion product.

[1] Similar effects have been observed on steel samples nickel- or nickel-
chromium-plated over zinc or cadmium underlays [485].
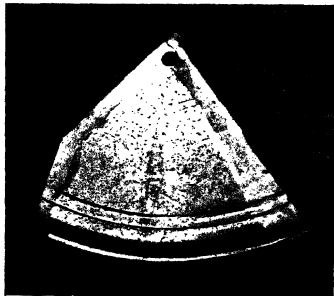
Atmospheric Exposure Test.
No. 62 : J 9
Copper-nickel-chromium Coat-
ing, on Zinc-base Die Casting.
β-type corrosion after 2 weeks.
FIG. 126.

× 1

Atmospheric Exposure Test.
No. 62 : J 9
Copper-nickel-chromium Coat-
ing, on Zinc-base Die Casting.
γ-type corrosion after 6 months :
numerous small patches of flaking.
FIG. 127.
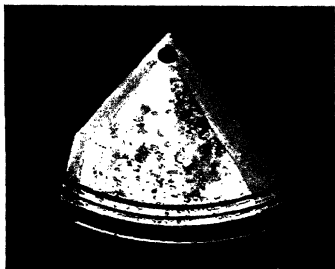
× 1
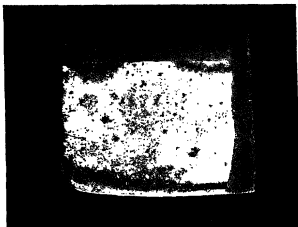
Atmospheric Exposure Test.
No. 64 : J 3
Nickel-chromium Coating on
Aluminium Alloy Casting.
β-type corrosion after 2 weeks.
FIG. 128.
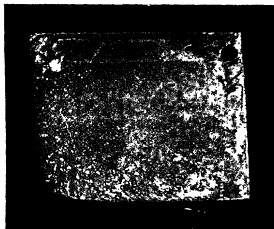
Atmospheric Exposure Test.
No. 64 : J 3
Nickel-chromium Coating on
Aluminium Alloy Casting.
γ-type corrosion after 6 months.
FIG. 129.

145

Sea-Water Immersion Tests (Table XVIII)

Reagent: a synthetic mixture of the following composition: sodium chloride 30 g., magnesium sulphate ($6H_2O$) 6·2 g., magnesium chloride ($6H_2O$) 4·4 g., calcium sulphate ($2H_2O$) 1·6 g., per litre. (The mixture corresponds approximately to the composition of North Sea water.) Each test piece (with all cut surfaces protected by a coating of paraffin wax) was suspended by a glass hook in an open jar containing 2 litres of the mixture. The solution was kept at about 1 cm. (0·4 in.) above the upper edge of the specimen, evaporation being compensated daily by addition of tap water: the solution was renewed once a month.

Duration of test: twelve months.[1]

Ferrous Samples. Corrosion by sea water was characterised in most cases by the formation, at the pores in the coating, of fine brown threads of corrosion product which gradually increased in size and formed nodules. In the highly porous coatings the whole surface of the specimen ultimately became covered with a thick bulky layer of brown rust. After removal of the corrosion product, many of the specimens showed pits and peeling of the coating. At the portions of the coating which remained unattacked, there gradually formed a dense crystalline greyish-white film consisting mainly of calcium carbonate, which protected the plating from further attack.[2]

Of the seventeen chromium-plated ferrous specimens, twelve showed peeling of the surface coating after only six months, and only three of the samples attained a figure of merit of 52. The individual results in this series of tests varied too widely to permit of a systematic correlation of the figure of merit with the thickness of the nickel underlay.

Fig. 130 shows the severity of the sea-water attack on No. 4 (E1) after six months' exposure. This specimen was rated γ after only three weeks.

No. 9 (G4) showed γ-type corrosion after only twelve weeks' exposure, and after six months was in the condition shown in Fig. 131. In addition to the corrosive attack and the peeling of the chromium coating, large areas of the surface were covered with a grey-white deposit consisting mainly of calcium carbonate.

Fig. 132 (No. 20: M1) is typical of α-type corrosion. Small threads and particles of rust are observed at the pores of the coating.

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[1] Immersion tests in the A.E.S.—A.S.T.M.—N.B.S. experiments [537] were of the intermittent type, comprising 1 minute in the solution and 14 minutes in air. The temperature was kept at 35° C. (95° F.) and the relative humidity at 60 ± 5 per cent.

[2] The formation of the calcium carbonate film is due to the use of tap water containing calcium carbonate for filling up the test vessels.

Sea-Water Immersion Test.
No. 4 : E 1
Copper-nickel-chromium Coating,
on Ferrous Base.
γ-type corrosion after 6 months.

Fig. 130.

Sea-Water Immersion Test.
No. 20 : M 1
Nickel-copper-nickel-chromium Coat-
ing, on Ferrous Base.
α-type corrosion after 1 month. Fine brown threads
and specks of rust at the pores on the coating.

Fig. 132.

× 1

Sea-Water Immersion Test.
No. 9 : G 4
Copper-nickel-chromium Coating, on Ferrous Base.
γ-type corrosion after 6 months.
Flaking and peeling of the chromium coating. Large areas of the surface covered with grey-white
film of calcium carbonate.

Fig. 131.

147

Basis Metal	Exterior Coating	Component	Serial No.	Mark	Thickness of Intercrustine Layers, μ		Thickness of Exterior Coating, μ		Sea-water Immersion — Condition of Surface						Fig. of Merit "G": weeks reqd. to produce γ-type corrosion	Sea-water Spray — Condition of Surface	Fig.	Fig. of Merit "G": days reqd. to produce γ-type corr.
							Nickel	Chrom.	after 1 mth.	Fig.	after 6 mths.	Fig.	after 12 mths.	Fig.				
Iron or Steel	Nickel Chromium	Ornamental hub cap	1	C7	Copper 3·0	Nickel —	5·0	—	β	—	γ	—	γ	—	14	Heavily rusted	139	5
		Radiator shell	4	B1	0·4	1·5	—	0·4	γ	—	γ	139	γ	—	3	—	140	5
		Cable protection tube	5	J11	0·2	4·0	—	0·6	β	—	γ	—	γ	—	7	—	—	5
		Gear handle	6	G11	0·2	7·0	—	0·6	β	—	γ	—	γ	—	22	—	—	5
		Radiator shell	7	F1	0·2	8·0	—	0·7	α	—	α	—	α	—	>52	—	—	30
		Shock absorber housing	8	G10	0·5	13·0	—	0·5	α	—	γ	—	γ	—	30	Heavily rusted	—	6
		Lamp bracket	9	G4	0·4	16·0	—	0·8	α	—	γ	131	γ	—	10		—	6
		Bonnet hinge	10	G18	0·5	22·0	—	0·5	α	—	α	—	α	—	>52		—	40
		Lamp bracket	11	G30	0·5	25·0	—	0·5	α	—	α	—	γ	—	30		—	14
		Bonnet screw	12	F4	0·3	37·0	—	0·5	α	—	γ	—	γ	—	17		—	7
		Lamp cross-bar	13	N3	5·0	8·0	—	0·5	β	—	γ	—	γ	—	14		—	5
		Lamp adjustion arm	14	G10	Brass 5·0	5·0	—	0·5	β	—	γ	—	γ	—	12	No test made	—	—
		Ventilating flap	15	E4	Zinc Not determinable 5·5	Brass 3·0	—	0·4	β	—	γ	—	γ	—	20	Heavily rusted	—	6
		Cap	16	K3	3·5	4·5	—		β	—	γ	—	γ	—	14	Not tested	—	—
		Hub disc	17	K6	4·5	5·0	—		β	—	γ	—	γ	—	18	Heavily rusted	—	6
		Beading	18	K10	4·0	8·0	—		β	—	γ	—	γ	—	18	rusted	—	4
		Bumper	19	G6	Nickel 7·0	Copper 6·0	Nickel 33·0	—	0·5	α	—	α	—	α	—	>52	Less heavily rusted	—	60
		Bumper	20	M1	7·0	35·0	2·0	—	0·75	α	132	α	—	α	—	50	Green effervescent patches	141	14
Brass	Nickel	Exterior door handle	21	A4	3 mths —		3·0	—	α	—	α	—	α	—	>52	Not tested	—	—
		Lamp fitting	22	C2			8·0	—	α	—	β	143	α	—	50	Yellow-white effervescent patches	—	25
		Running-board rail	23	C1			3·0	—	α	134	α	—	β	—	>52	Yellow-white effervescent patches	142	23
Brass	Chromium	Radiator shell	25	G1	Nickel 2·5		—	0·5	α	—	α	—	α	—	>52	Yellow-white effervescent patches	—	25
		Badge	26	J5	2·5		—	0·5	α	—	α	—	γ	—	39	Not tested	—	—
		Radiator screw cap	27	K11	2·5		—	0·4	>α	—	α	—	β	—	>52	Yellow-white effervescent patches	—	33
		Ornamental hub cap	29	K7	2·5		—	0·8	α	—	α	—	α	—	>52	Yellow-white effervescent patches	—	54
		Stop lamp	30	G15	3·5		—	0·5	α	—	β	—	β	—	>52	Not tested	—	—
		Cable protection tube	31	J11	3·5		—	0·5	α	—	α	—	α	—	>52	Yellow-white effervescent patches	—	33
		Hub cap	32	M2	4·0		—	0·5	α	—	α	—	α	—	>52		—	54
		Radiator shell	33	M3	4·5		—	0·4	α	—	α	—	α	—	>52		—	25
		Footboard plate	34	F3	4·5		—	0·4	α	—	α	—	α	—	>52			
		Nut	35	G14	4·5		—	0·5	α	—	α	—	α	—	>52	Not tested		
		Cup	36	J4	4·5		—	0·5	α	—	β	—	β	—	>52			
		Lamp casing	37	C5	5·0		—	0·5	α	—	α	—	α	—	>52	Yellow-white effervescent patches	—	25
		Bonnet-support rail	38	C13	5·0		—	0·5	α	—	α	—	α	—	>52		—	33
		Radiator shell	39	N1	5·0		—	0·5	α	—	α	—	α	—	>52	patches	—	54
		Hub cap	40	N2	5·0		—	0·5	α	—	β	—	γ	—	50	Yellow-white effervescent patches	—	21
		Beading	41	K10	6·5		—	0·4	α	—	α	—	α	—	>52	effervescent patches		
		Bonnet screw	43	K8	12·5		—	0·5	γ	—	γ	—	γ	—	11	Not tested		
		Lamp casing	44	G3	14·0		—	0·7	>α	—	α	—	α	—	>52	Yellow-white effervescent patches	—	54
		Knob	46	G13	Copper 0·5	Nickel 2·5	—	0·6	α	—	α	—	α	—	>52	Not tested		
		Ornamental hub cap	47	G3	0·5	3·5	—	0·8	α	—	α	—	α	—	>52			
		Ornamental hub cap	48	F2	0·4	4·0	—	0·7	α	—	α	—	α	—	>52	Yellow-white effervescent patches	—	40
		Radiator shell	49	H	2·5	4·5	—	0·5	α	—	α	—	α	—	>52	patches	—	54
		Windscreen column	50	G17	0·3	4·5	—	0·6	α	—	α	—	α	—	>52	Not tested		
		Reading rod	51	J6	0·6	9·0	—	0·5	α	—	α	—	α	—	>52			
Bronze	Chromium	Rail	52	F5	Zinc 120		—	0·5	α	—	α	—	β	—	39	Not tested		
		Handle	53	B2			—	1·5	α	—	γ	—	γ	—	22	Not tested		
		Steering-column bracket	54	B3			—	1·5	α	—	γ	—	Tests discontinued after 6 months		20	Blue-grey effervescent patches	143	14
		Roller bearing	55	B5			—	1·5	α	—	γ	—			22	Not tested		
		Steering-column bracket	56	B4			—	2·6	γ	—	γ	135			17	blue-grey effervescent patches	—	19
		Lock	57	B1			—	3·6	γ	—	γ	—			26	Not tested		
Zinc-base Die Castings	Nickel	Exterior door handle	58	A1	1 mth		2·0	—	γ	136	γ	—	Tests discontinued after 6 months		—	Yellow-white effervescent patches	144	5
		Interior door handle	59	A3			2·2	—	γ	—	γ	—			6	Yellow-white effervescent patches	145	5
	Chromium	Exterior door handle	60	A2	Nickel 2·0		—	0·3	β	137	γ	—			6	patches		
		Radiator mascot	61	J1	Copper 0·5	Nickel 4·0	—	0·5	β	—	α	—	α	—	4	Not tested		
		Radiator screw cap	62	J9	0·4	2·5	—	0·6	γ	138	γ	—	γ	—	4	Not tested		
		Radiator screw cap	63	E2	Brass 0·3	Nickel 1·8	—	0·5	γ	—	γ	—	γ	—	4	Not tested		
Aluminium Alloy Casting	Chromium	Bracket	65	J8	Nickel 4·0		—	0·4	α	—	α	—	γ	—	50	Yellow-white effervescent patches	146	5

Brass Samples. Both the chromium- and the nickel-plated brass samples showed surprisingly good behaviour under sea-water attack. The minimum grading (α) was not required until after three months.
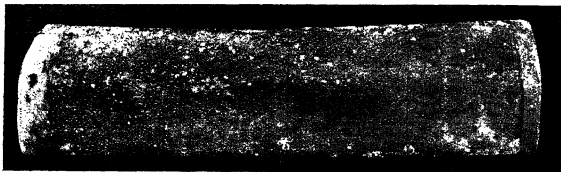
Sea-Water Immersion Test.
No. 22 : C 2.
Nickel Coating, on Brass.
β-type corrosion after 6 months.
(Condition after removal of patches of white corrosion product.)
FIG. 133.

Out of twenty-eight samples, twenty-three attained a figure of merit of > 52, and two a rating of 50.

Corrosion of the brass-base samples was characterised by the formation of yellow-white spotty excrescences at the pores on the surface coating. After six months' exposure, on removal of the corrosion product, only five samples showed slight surface attack (β) and in only four of these samples did the corrosion develop to the γ grade.

Fig. 133 shows the nickel-plated sample No. 22 (C2) after six months' exposure. After the spots of corrosion product had been wiped off, the specimen showed only " moderate " corrosion (β).

No. 23 (C4), directly chromium-plated, showed spotty white excrescences after only three months (Fig. 134). The patches could, however, easily be wiped off and after their removal the chromium coating was practically spotless and intact, meriting the α rating.

Sea-Water Immersion Test.
No. 23 : C 4
Chromium Coating, on Brass.
α-type corrosion after 3 months.
FIG. 134.

Twelve months' exposure was required to produce signs of permanent spotting (β).

In the course of the first month's exposure, crystalline adherent films of calcium carbonate formed on some of the specimens and the plating in those areas became matt, but the effect was not accompanied by any actual corrosion attack. The copper-nickel-chromium-plated samples 46–51 showed highly satisfactory resistance, attaining a figure of merit of > 52. The small yellow-white patches of corrosion product formed could easily be wiped off, leaving the surface entirely intact. Some of these samples also showed the grey-white adherent film of calcium carbonate referred to above.

Bronze Samples. The (directly-chromium-plated) bronze-base samples showed outstandingly poor resistance to sea-water attack. Incipient corrosion was characterised by the formation of blue-green patches at the pores of the coating, and after about four months, flaking
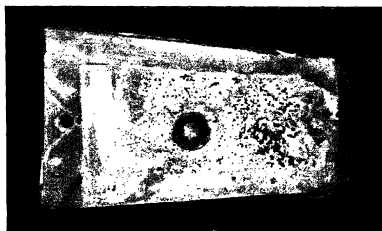
Sea-Water Immersion Test.
No. 56 : B 4.
Chromium Coating, on Bronze.
γ-type corrosion after 6 months.
Extensive flaking of the chromium coating.

Fig. 135.

and peeling (γ-type corrosion) occurred on all the samples. The severity of the attack was such as to necessitate discontinuance of the tests after six months. Fig. 135 shows the surface of No. 56 (B4) ; the flaking and peeling of the coating is clearly visible.

Zinc-base Die Castings. The zinc-base samples were very rapidly corroded in the sea-water tests. After only a short period of immersion, white spots appeared at the pores and rapidly spread. After three to six weeks the coating scaled off. At the areas which were free from porosity the samples became covered with a film of calcium

carbonate.   Fig. 136 shows No. 58 (A1) after one month : on removal
of the patches of corrosion product, cracks were observed on the nickel
plating.   Fig. 137 shows β-type corrosion in the nickel-chromium-plated
sample A2 after one month ; after six weeks, scaling of the chromium

× 1

Sea-Water Immersion Test.
No. 58 : A 1
Nickel Coating, on Zinc-base Die Casting.
β-type corrosion after 1 month : nodular blisters.
FIG. 136.

coating was observed (γ).   Fig. 138 shows No. 62 (J9), in which incipient
scaling occurred after three weeks.

Aluminium Alloy Castings.   Only one specimen of this type,
No. 65 (J8), was submitted to test.   This sample offered consider-
ably better resistance to sea-water attack than the zinc-base parts.   The
surface became covered with a crystalline white film of calcium carbonate
and small isolated patches of yellow-white corrosion product were
observed.   No scaling of the chromium coating (γ) was observed until
after fifty weeks.

Sea-Water Spray Tests (Table XVIII)

The experimental conditions were those developed by the D.V.L.
[260].[1]   The spray nozzles were of Bakelite and the specimens were
suspended by string from glass hooks.   The spray was applied, under a
pressure of 2 atmospheres, for 10 minutes per hour ; the mist did not
entirely clear within the hour.   Spraying was carried out in working
hours only ; the cycle was therefore 8 hours, in which spray was applied
during 10 minutes of each hour, and 16 " dry " hours.   It is believed that

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[1] This paper contains a detailed report of a study of methods of accelerated
corrosion testing, carried out under the ægis of the Deutsches Verein für Luftfahrt.
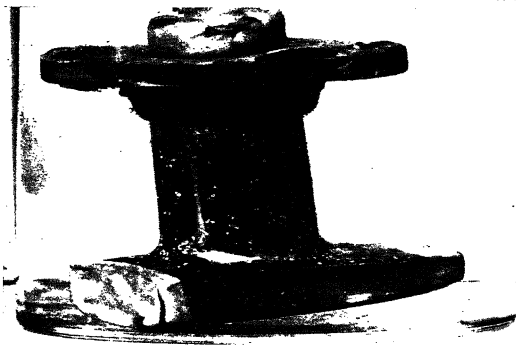
Sea-Water Immersion Test.
No. 60 : A 2
Nickel-chromium Coating, on Zinc-base Die Casting.
β-type corrosion after 1 month.
FIG. 137.

Sea-Water Immersion Test.
No. 62 : J 9
Copper-nickel-chromium Coating, on Zinc-base Die Casting.
γ-type corrosion after 3 weeks : blistering and incipient peeling of the coating.
FIG. 138.
153

such alternations of "spray" and "dry" cycles may represent a specially close approximation to service conditions.[1]

Sea-water spray constitutes a very searching test for metal coatings, embodying in concentrated form the types of attack present in both atmospheric exposure and sea-water immersion. In the spray test, the specimens are constantly in a saline atmosphere which is saturated with moisture, and to which there is unimpeded access of oxygen ; the fact that the corrosion products are not swept away but can settle on the specimen further enhances the attack. Disintegration (γ-type attack) therefore takes place in an appreciably shorter period than under any other form of corrosion test used. In this series of tests, the figure of merit (G) is taken as the number of *days* to observation of peeling and flaking of the coating (see Table XVIII).

× 1
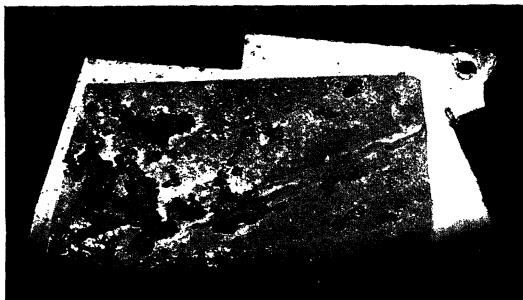
Sea-Water Spray Test.
No. 1 : C 7
Copper-nickel Coating, on Ferrous Base.
Condition after 5 days.

FIG. 139.

[1] Wernick [540] gives details of a specification for cadmium plating in which it is laid down that the "normal spraying" test shall consist of alternating periods of 8 hours spraying followed by a 16-hour "off" period, during which no spraying will occur but the samples will remain in the atmosphere of the salt-spray chamber. This intermittent type of test is specified as being "more convenient and also likely to result in a closer assessment of the value of the deposit." Bannister [482], summarising methods of spray testing adopted by various investigators, states that "for attempting to reproduce working conditions, the use of the intermittent spray test is usually sounder, because during the drying periods it allows for the action of corrosion products already formed" (see also p. 130). The American Society for Testing Materials (in conjunction with the American Electroplaters' Society) recommends continuous spray tests of 48 and 16 hours' duration, for coatings designed to withstand, respectively, general and mild conditions (p. 42). See also 546.

Ferrous Samples. After only a few days, clearly defined patches of rust appeared at the pores; these spread rapidly and ultimately resulted in peeling of the coating. Of the sixteen samples examined, only three (Nos. 7, 10, 19) withstood the attack for a period longer than fourteen days. The best results were given by No. 19, which had a nickel underlay of 44 μ (G = 60 days). In the case of the other samples in this series, no clear relationship could be established between thickness of nickel underlay and resistance to corrosion.
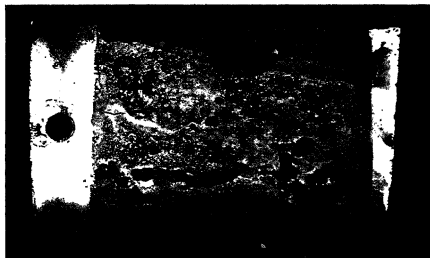
Sea-Water Spray Test.
No. 4 : E 1
Copper-nickel-chromium Coating, on Ferrous Base.
Condition after 5 days.
FIG. 140.

Sea-Water Spray Test.
No. 20 : M 1
Nickel-copper-nickel-chromium Coating, on Ferrous Base.
Condition after 14 days.
FIG. 141.

Fig. 139 shows the nickel-plated sample No. 1 (C7) after five days. The surface is covered with clearly marked nodules of rust and the coating is peeling off in several places.

Fig. 140 shows a similar condition in the copper-nickel-chromium-plated sample No. 4, also after five days.

No. 20 (M1), nickel-chromium-plated over a thick copper underlay (35 μ), gave somewhat better results (Fig. 141, after fourteen days). In addition to the rust deposit, green patches of copper salts were observed.

Brass Samples. As in all the other corrosion tests, the brass-base samples showed the best behaviour in the salt spray : the figure of merit varied from twenty-one to fifty-four days. Yellow-white

Sea-Water Spray Test.
No. 23 : C 4
Chromium Coating, on Brass.
Condition after 33 days.
FIG. 142.

patches of corrosion product formed an initial attack, and underneath these patches the coating gradually flaked off. Fig. 142 is typical of all the brass-base samples.

Bronze Samples. The behaviour of these samples was similar to that of the brass-base specimens, except that the corrosion product on the bronze specimens was of a bluish-green colour.

The figures of merit of the two samples examined (Nos. 54 and 56 ; rating 14 and 19 respectively) were at the lower end of the range of values attained by the brass samples. Fig. 143 (No. 54 : B3, after fourteen days) shows the blue-green corrosion patches and the flaking of the coating. Results on No. 56 were similar.

Zinc- and Aluminium-base Alloys. As was to be anticipated, both the zinc- and the aluminium-base specimens withstood the test for only a very short period (G = 5 days). Patches of yellow-white cor-

rosion product rapidly formed and spread over the whole surface.
After about five days the coating peeled away (G = 5 days).[1]   Typical
effects are shown in Figs. 144–146.
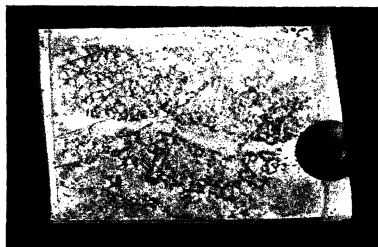
Sea-Water Spray Test.
No. 54 : B 3
Chromium Coating, on Bronze.
Condition after 14 days.
FIG. 143.

× 1
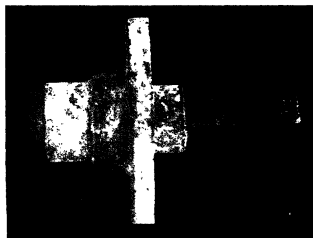
Sea-Water Spray Test.
No. 58 : A 1
Nickel Coating, on Zinc-base Die Casting.
Condition after 5 days.
FIG. 144.

[1] Thompson and Jelen [470], reporting on zinc coated with different thicknesses of nickel and then with different thicknesses of chromium, tested by immersion in 20 per cent. sodium chloride and 5 and 10 per cent. ammonium sulphate solutions, state that " life is proportional to the thickness of the underlying nickel, and independent of the thickness of chromium up to a thickness of 0·00014 inch." [See also 379 and 478.]
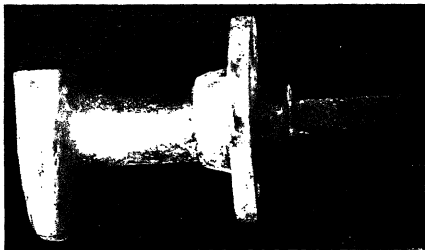
Sea-Water Spray Test.
No. 60: A 2
Nickel-chromium Coating, on Zinc-base Die Casting.
Condition after 5 days.

FIG. 145.
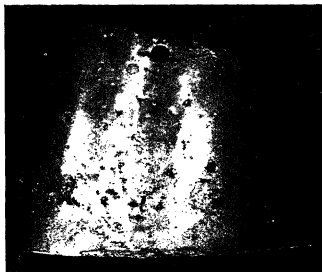
Sea-Water Spray Test.
No. 65: J 8
Nickel-chromium Coating, on Aluminium Alloy Casting.
Condition after 5 days.

FIG. 146.

Summary of the Atmospheric, Sea-Water Immersion and Sea-Water Spray Tests

In assessing atmospheric exposure tests, it must be borne in mind that the results are vitally affected by the period of the year at which the

exposure takes place, the type of climate, and other variable factors.[1] In order to eliminate as far as possible the effect of such climatic variables, it was arranged that the exposure tests described above should be of a year's duration (March 1, 1932, to February 28, 1933) in order that all types of weather peculiar to spring, summer, autumn and winter should operate on the specimens.

In sea-water immersion and in spray tests, on the other hand, external variables are eliminated and the conditions are kept constant as to atmosphere and temperature. Due precaution must therefore be observed in making comparison between the results of the different series of tests.

Atmospheric Exposure.

1. As shown in Fig. 117, the results of the tests on the ferrous samples coated with copper-nickel-chromium showed a clear relationship between the thickness of the nickel layer and the figure of merit attained by the specimen. Increase in thickness of the nickel underlay was accompanied by marked increase in life. No. 20, which had a very thick (35 μ) layer of copper, and a thin layer of nickel, also showed a relatively long life (G = 39), but did not equal the high rating obtained by No. 19 (G = $>$ 52) which had a total *nickel* underlay of 7 + 33 μ. (In connection with the relative value of copper and nickel underlays, see p. 221.)

The practical conclusion from the tests is that in the chromium plating of iron and steel the factor of primary importance is a thick underlay of nickel [191, 398, 485].[2]

2. Irrespective of the nature and thickness of the underlay(s) used, chromium plating on a brass base showed considerably higher resistance to corrosion than on a ferrous base. Fig. 147, which shows the frequency of rating of the respective groups, very clearly indicates the superiority of the brass-base specimens. The thickness of the nickel underlay on the brass samples varies too slightly to permit of any conclusion with respect to its influence on corrosion resistance (see, however, p. 211).

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[1] Data on typical effects of seasonal variations in identical locations are cited by Blum and co-workers [485].

The A.E.S.—A.S.T.M.—N.B.S. atmospheric tests comprised exposure in five locations, typical, respectively, of (1) tropical marine atmosphere, (2) industrial urban atmosphere, (3) severe industrial atmosphere, (4) slightly contaminated northern marine atmosphere, (5) uncontaminated rural atmosphere, (6) typical suburban atmosphere. Over 100 inspections were made at the six locations during the two-year period : the conclusions (see summary, p. 220) are based on over 100,000 individual ratings of specimens.

[2] This conclusion is in agreement with that drawn by the American investigators [485], who state : "The total thickness of nickel (or copper and nickel) is the most important factor in protective value, regardless of whether or not chromium is also applied. . . . It is evident that the most practical way of increasing the protective value of nickel deposits is to increase their thickness."

3. The few bronze samples, which were all directly-chromium-plated, showed very irregular behaviour. The results, however, lead to the assumption that an underlay of nickel is advantageous (see also p. 199)

4. The coatings on the zinc- and aluminium-alloy samples suffered very rapid deterioration under atmospheric conditions. These materials are unsuitable for parts exposed to rain, snow, etc., but may be used for interior fittings in positions in which they are shielded from direct access of moisture.

5. Due to the paucity of material, the results of this series of tests do not provide sufficient data for assessment of the weathering properties of nickel coatings.
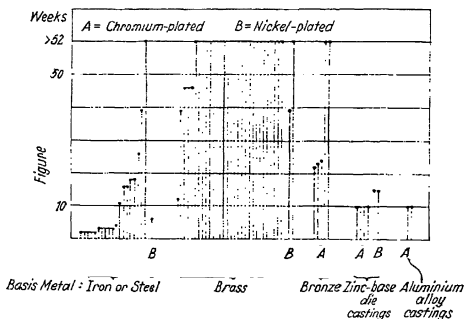
FIG. 147.—Atmospheric Exposure Tests. Summary of Results.

Sea-Water Immersion.

1. The relationship between thickness of nickel underlay and resistance to corrosion established in the atmospheric exposure tests was not so clearly demonstrated in the sea-water immersion tests.

Fig. 148 gives a summary of the results, arranged in order of merit, without regard to the nature and thickness of the underlay(s) used. A comparison of Figs. 147 and 148 reveals the superior resistance of the ferrous-base samples to sea water, as compared with their behaviour under atmospheric exposure. In this connection it may be pointed out that although, *per se*, sea-water is indubitably a more corrosive medium than rain-water, dew, etc., the nature of the attack under atmospheric conditions is more drastic than that imposed by a stagnant liquid electrolyte. Under atmospheric conditions, the majority of the ferrous ions going into solution are oxidised *in situ* and are precipitated as rust.

On dry days the rust hardens and on wet days it softens and facilitates the penetration of moisture and atmospheric oxygen under the coating : the corrosion product gradually swells and ultimately causes scaling and peeling of the coating.

In a liquid medium, only a very small proportion of the metal ions going into solution is precipitated *in situ*. Due partly to movement of the electrolyte and partly to diffusion, they are carried away and are oxidised elsewhere. The rust formed is bulky and soft and does not endanger the coating to so great an extent as the deposit built up by drying, re-wetting and gradual hardening during atmospheric exposure. Under conditions of stagnant liquid attack, peeling of the coating is therefore correspondingly delayed.
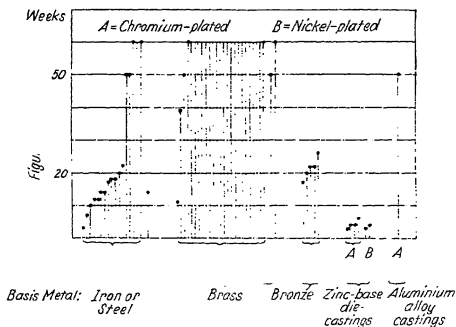
FIG. 148.—Sea-Water Immersion Tests. Summary of Results.

2. In sea-water, as in atmospheric tests, the brass-base samples withstood the attack very much better than the ferrous-base specimens (Fig. 148).

3. Bronze samples chromium-plated without an underlay showed very poor resistance to corrosion. All the results reported indicate the inadvisability of direct deposition of chromium on bronze.

4. The remarks relating to zinc- and aluminium-alloy samples in the atmospheric tests (*vide supra*) apply also to their behaviour in the sea-water tests. The zinc-base specimens were especially severely attacked.

Sea-Water Spray.

The data in Fig. 149 are arranged on the same basis as those reported for the atmospheric and sea-water immersion tests (Figs. 147 and 148),

but in the spray tests the figure of merit is given in *days* instead of *months*. These tests also indicate a certain superiority on the part of the brass-base samples.
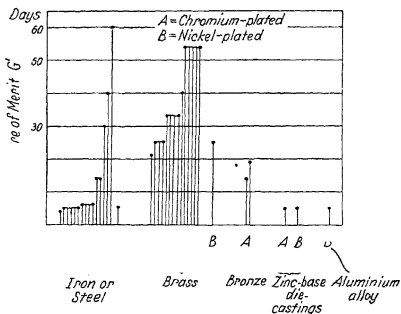
FIG. 149.—Sea-Water Spray Tests. Summary of Results.

Tests against Polishing Mixtures, Fuels, Oils and Greases, Radiator-sealing Mixtures, Anti-freeze Compounds (Table XIX)

Polishes. The polishes were ordinary commercial products; exact details of composition are not known. The polish was applied each day by means of a soft brush. The specimens were cleaned once a week and examined with reference to surface condition. Duration of test : twelve months.

Fuels. The fuels were typical commercial products, purchased in the open market ; no analyses were made. The tests were made in open vessels, the specimens being half-immersed in the liquids. Evaporation was compensated each day, the required amount of the solution being allowed to run over the uncovered portion of the test piece as it passed into the vessel. This method was adopted in order to simulate service conditions, in which the metal coatings are only inter-mittently in contact with the fuel mixtures. The specimens were cleaned once a month, their surface condition was examined and the vessels were filled with fresh liquid. Duration of test : twelve months.

Oils and Greases. The oils and greases, also commercial pro-ducts, were applied by means of a soft brush. The specimens were cleaned and examined once a week. Duration of test : twelve months.

Radiator-cleaning, Radiator-sealing and Anti-freeze Mix-tures. All the substances used were commercial products ; no details

of composition are available.   The mixtures were dissolved in water, as recommended by the respective suppliers, and the tests were made in open vessels.   The specimens were cleaned and examined once a month, and the liquid in the vessels was renewed.   The radiator-sealing mixture was applied to the specimens by means of a soft brush, in accordance with instructions supplied for service use.

The coatings used in the tests were: No. 7, F1, copper-nickel-chromium-plated steel, and No. 25, G1, nickel-chromium-plated brass.

TABLE XIX.

TESTS ON CHROMIUM COATINGS EXPOSED TO LIQUID FUELS, OILS, POLISHING MIXTURES, ETC.

Corrosive Medium.	Surface Condition after 12 months.	
	No. 7 : F1.	No. 25 : G1.
	Steel Base : Copper-nickel-chromium Coating.	Brass Base : Nickel-chromium Coating.
Motor Fuels (4 varieties)	Chromium coating unattacked: in some cases brownish-green deposit was formed	
Oils (8 varieties) . . .	Unchanged	Unchanged
Greases (3 varieties) . .	Unchanged	Unchanged
Polishing Mixtures (6 varieties)	Unchanged	Unchanged
Radiator-cleaning Mixtures (3 varieties)	In one case an adherent grey-white coating and in two cases a brownish-green deposit had formed. In all cases the chromium coating remained free from attack	
Radiator-sealing Mixtures (3 varieties)	In two cases a grey surface deposit had formed, but the chromium coating remained free from attack. In the third case the surface appearance was unchanged	
Anti-freeze Mixture .	A grey-white surface deposit had formed, but the chromium coating was unattacked	

The results (Table XIX) show that neither the chromium coating nor the metal(s) of the underlays had been attacked by the oils, greases or polishing compounds.   The chromium plating was also completely

immune from attack by the fuel mixtures ; the brownish-green deposit which appeared on some of the samples is believed to be due to slight interaction, through the pores of the outer coating, of the corroding medium and the underlay material.   [In confirmation of these results see 240.]   The grey-white or brownish-grey deposit found on samples

× 1
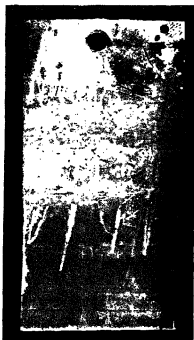
No. 7 : F 1

Copper-nickel-chromium
Coating, on Ferrous
Base.

After 12 months' exposure to
the action of a commercial
radiator cleaning mixture.

FIG. 150.

which had been in contact with sealing and anti-freeze mixtures is presumably due to decomposition of constituents of the respective compounds.   (Fig. 150 shows No. 7 after exposure for twelve months to a cleaning mixture ; after removal of the corrosion product the chromium plating was found to be free from any form of attack.)

TESTS ON EXPERIMENTAL CHROMIUM-PLATED SAMPLES

In view of the wide variation in type and thickness of plating and of the many other variables associated with the coatings on the automobile components, only very tentative conclusions could be drawn from the foregoing tests with regard to optimum underlay material and optimum thickness of chromium coating. It was therefore decided to carry out supplementary tests on chromium plating deposited under known and accurately controlled conditions, on samples in which the (sheet) form should ensure, as far as possible, uniform thickness of both the chromium coating and the underlays.

The materials selected as foundations for the experimental samples were similar to those actually used in automobile components, viz. iron and mild steel, brass, bronze, zinc-base and aluminium alloy castings.

Thickness of Coating

The thickness of deposit was calculated from conditions of deposition ; subsequent examination of the specimens showed that the nominal figures were in most cases correct.

Regularity of Coating

Some of the specimens were unsatisfactory in this respect. Variations of 10–20 per cent. were found on individual specimens, while between different samples the discrepancies were even greater. A possible variation of 50 per cent. should be allowed for in extreme cases.

Surface Condition

Colour and Lustre. In general, the experimental samples were entirely satisfactory in this respect. Microscopical examination showed the amorphous structure characteristic of good bright-chromium-plating (Fig. 151). Samples on which the chromium had been deposited over a copper underlay had a somewhat lower lustre and were dark in colour. The ferrous samples chromium-plated with a thin underlay of copper (group IIa) were semi-matt and under the microscope showed clearly defined polishing scratches (Fig. 152). Those on which a thicker underlay of copper had been used (IIb ; copper 5 μ). and the sample

TABLE XX.—TYPE AND CONDITION OF EXPERIMENTAL SAMPLES

Basis Metal.	Description of Test Piece. Type of Coating.	Mark.	Type and Thickness of Intermediate Layers, μ			Thickness of Exterior Chromium Coating, μ	Surface Condition of Coating.	Fig.
			Brass.	Copper.	Nickel.			
	Chromium	I	—	—	—	2–3	Highly lustrous	151
	Copper-Chromium	IIa	—	0·2–0·5	—	0·5	Semi-matt : pronounced polishing scratches	152
		IIb	—	5	—		Slightly dull	—
	Nickel-Chromium	IIIa	—	—	5	0·5	Highly lustrous	—
		IIIb	—	—	15			
		IIIc	—	—	25			
	Nickel-Chromium (after Coppering Cleaning)	IV	—	Cleaned in a coppering solution	15	0·5	Highly lustrous : slightly porous	—
Iron or Steel	Copper-Nickel-Chromium	Va	—	0·2–0·5	5	0·5	Highly lustrous	—
		Vb	—		15			
		Vc	—		25			
		Vd	—	5	5			
		Ve	—		15			
		Vf	—		25			
	Brass-Nickel-Chromium	VIa	0·2–0·5	—	5	0·5	Highly lustrous	—
		VIb		—	15		,, ,, : slightly porous	—
		VIc		—	25		,, ,, ,,	153
		VId	5	—	5		,, ,, : nodular " warts "	—
		VIe		—	15		,, ,, : slightly porous	—
		VIf		—	25		,, ,, ,,	—
	Nickel-Copper-Chromium	VII	Nickel 5	Copper 5	—	0·5	Slightly dull	—

Material	Deposit combination	Code	Zinc	Brass / Copper	Nickel	Chromium	Appearance	Ref.
	Nickel-Copper-Nickel Chromium	VIII	Zinc 5	Brass 5	15	0·5	Highly lustrous	—
	Zinc-Brass-Nickel-Chromium	IX	Zinc 5	Brass 5	15	0·5	Highly lustrous	—
	Chromium . . .	1	—	—	—	2–3	Highly lustrous: cracked in places	154
Brass	Nickel-Chromium . . .	IIIa, IIIb, IIIc	—	—	5, 15, 25	0·5	} Highly lustrous	—
Brass	Copper-Nickel-Chromium	Va, Vb, Vc, Vd, Ve, Vf	—	Copper 0·2–0·5; 5	5, 15, 25; 5, 15, 25	0·5	} Highly lustrous	—
Bronze	Nickel-Chromium . . .	IIIa, IIIb, IIIc	—	—	5, 15, 25	0·5	} Highly lustrous: porous	—, 155
Bronze	Nickel-Chromium . . .	IIIa, IIIb, IIIc	—	—	5, 15, 25	0·5	} Highly lustrous: porous	—
Zinc-base Die Castings	Copper-Nickel-Chromium	Va, Vb, Vc	—	Copper 0·2–0·5	5, 15, 25	0·5	} Highly lustrous: porous	—
Zinc-base Die Castings	Brass-Nickel-Chromium	VIa, VIb, VIc	0·2–0·5	0·2–0·5	5, 15, 25	0·5	} Highly lustrous: porous	—
Aluminium Alloy Castings	Nickel-Chromium . . .	IIIa, IIIb, IIIc	—	—	5, 15, 25	0·5	Highly lustrous: porous; showed indications of burning	156, —, —

plated with a nickel-copper underlay were slightly lacking in lustre. The
examination of these specimens confirmed the earlier conclusions with
respect to the influence of the basis metal on the colour and lustre of
the chromium plating (see p. 48). The results also indicate that with

× 200

Chromium Coating (2–3 μ) deposited without underlay on Ferrous
(Typical of high-grade bright chromium plating: showing slight polishing scratches.)
Fig. 151.

× 200
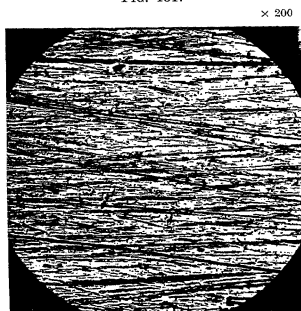
Copper-chromium Coating, on Ferrous Base.
(Typical of semi-matt chromium plating: showing pronounced polishing scratches.)
Fig. 152.

both ferrous and brass bases it is possible, if conditions of deposition
are correct, to obtain bright plating even with directly deposited thick
coatings of chromium.

Surface Defects. In no case had any portion of the experimental samples escaped plating nor had the plating in any case been polished away.

Warts (nodules) were observed on the brass-nickel-chromium-plated ferrous sample VI*d* only (Fig. 153); at these points the

× 50

Brass-nickel-chromium Coating, on Ferrous Base.
(Showing nodular " wart " formation.)
FIG. 153.

× 200
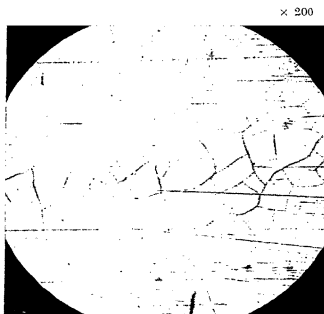
Chromium Coating (2–3 μ), on Brass.
(Typical of bright chromium plating: showing stress cracks.)
FIG. 154.

plating had a matt appearance. In some cases the chromium coatings on the bronze, zinc-, and aluminium-base samples showed very marked porosity (Fig. 155), the defect being due mainly to the porous character of the basis material. (*Note* : " porosity " here indicates

*macro*scopically visible porosity which constitutes a definite surface defect.) The coatings on a few of the ferrous-base specimens were slightly porous (groups IV and VI), but those on the brass samples were entirely free from porosity. The brass samples chromium-plated with-

× 200
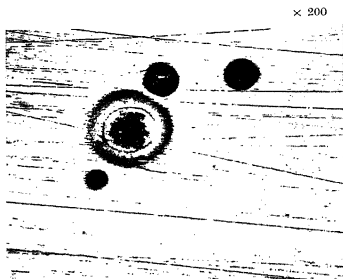
Nickel-chromium Coating, on Bronze.
(Typical of highly porous chromium plating.)
Fig. 155.

× 200
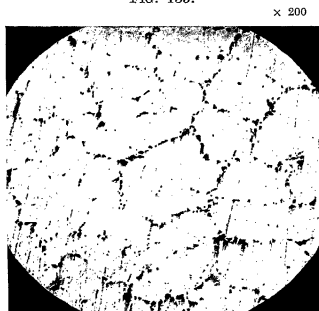
Nickel-chromium Coating, on Aluminium Alloy Casting.
(Showing porosity and indications of " burning.")
Fig. 156.

out an underlay were the only specimens showing cracks in the coating (Fig. 154), thus confirming earlier results which indicated the tendency of thick deposits of chromium to crack, due to internal stress. The chromium plating on the aluminium-alloy samples showed signs of " burning " (Fig. 156).

Adhesion and Capacity for Deformation

The ferrous- and brass-base samples were tested by the close-bend test, as used for the automobile components (p. 66) ; the bronze, zinc and aluminium alloy specimens were examined by means of the ball indentation test, a load of 3000 kg. and a ball of 10 mm. dia. being used on all except the aluminium-base samples, for which, on account of the softness of the base, a load of 1000 kg. was employed.

Close-bend Tests (Table XXI).

Cracking. The lowest bending capacity was shown by ferrous and brass specimens carrying a heavy direct chromium plating, confirming the earlier conclusions with reference to the inferior bending properties of thick chromium coatings.
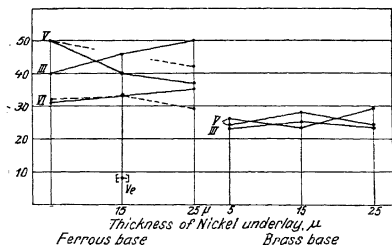
FIG. 157.—Close-Bend Tests on Experimental Samples.

In general, the bending capacity of ferrous-base specimens was superior to that of the brass-base samples. Copper-chromium and nickel-copper-chromium coatings, which gave the best results, could be bent to radii of 0·3–0·4 mm. before cracking set in. On nickel-chromium-plated specimens, cracking occurred at much larger radii. No relationship could be established between the thickness of nickel underlay and behaviour in the close-bend test (see Fig. 157 : comparative data on samples bearing nickel underlays 5, 15 and 25 μ thickness). Fig. 158 shows the fine cracks on sample IV, which had been chromium-plated on a nickel underlay deposited over a copper strike.

Flaking of the Chromium Coating. In a large number of the nickel-chromium-plated ferrous specimens, flaking of the chromium coating occurred at certain bending radii (see Fig. 159, sample VI*d*,

TABLE XXI.—CLOSE-BEND ADHESION TESTS ON EXPERIMENTAL SAMPLES

Basis Metal	Type of Coating	Mark	Brass (μ)	Copper (μ)	Nickel (μ)	Thickness of Exterior Chromium Coating, μ	Thickness of Specimen (d), mm.	Bending Radius (r), mm.	Ratio $\frac{2r}{a}$	Bend Value $\frac{100a}{2r+a}$	Condition of Test Piece at Point of Sharpest Bend.	Fig.
Iron or Steel	Chromium	I	—	—	—	2-3	1	1.9	3.8	21	Fine cracks	—
	Copper+Chromium	IIa	—	0.2-0.5	—	0.5	1	0.3	0.6	63	Fine cracks	—
		IIb	—	5	—	0.5	1	0.3	0.6	63	,,	—
	Nickel+Chromium	IIIa	—	—	5	0.5	1	0.75	1.5	40	Fine cracks and slight flaking	—
		IIIb	—	—	15	0.5	1	0.60	1.2	46	,,	—
		IIIc	—	—	25	0.5	1	0.50	1.0	50	,,	—
	Nickel+Chromium (after coppering-cleaning)	IV	—	Cleaned in a coppering solution	15	0.5	1	0.55	1.1	48	Fine cracks	158
	Copper+Nickel+Chromium	Va	—	0.2-0.5	5	0.5	1	0.50	1.0	50	Fine cracks	—
		Vb	—	0.2-0.5	15	0.5	1	0.75	1.5	40	Peeling	160
		Vc	—	0.2-0.5	25	0.5	1	0.85	1.7	37	Fine cracks	—
		Vd	—	5	5	0.5	1	0.75	1.5	50	Severe peeling	—
		Ve	—	5	15	0.5	1	6.0	12.0	8	Fine cracks and slight flaking	—
		Vf	—	5	25	0.5	1	0.70	1.4	42	Fine cracks and severe flaking	—
	Brass+Nickel+Chromium	VIa	0.2-0.5	—	5	0.5	1	1.1	2.2	31	Fine cracks and severe flaking	159
		VIb	0.2-0.5	—	15	0.5	1	0.95	1.9	33	,, ,, ,, slight	—
		VIc	0.2-0.5	—	25	0.5	1	1.05	2.1	33	,, ,, ,, severe	—
		VId	5	—	5	0.5	1	1.05	2.1	32	,, ,, ,, slight	—
		VIe	5	—	15	0.5	1	1.0	2.0	33	,, ,, ,, severe	—
		VIf	5	—	25	0.5	1	1.2	2.4	29	Fine cracks	—
	Nickel+Copper+Chromium	VII	—	5	5	0.5	1	0.4	0.8	56	Fine cracks	—
	Nickel+Copper+Brass+Chromium	VIII	5	5	15	0.5	1	1.15	2.3	30	Fine cracks and slight flaking	—
	Zinc+Brass+Nickel+Chromium	IX	1	Zinc 5	15	0.5	1	1.1	2.2	31	Fine cracks	—
	Chromium	I	—	—	—	2-3	1	2.4	4.8	17	Fine cracks	—
	Nickel+Chromium	IIIa	—	—	5	0.5	1	1.65	3.3	23	Fine cracks	—
		IIIb	—	—	15	0.5	1	1.5	3.0	25	,,	—
		IIIc	—	—	25	0.5	1	1.65	3.3	21	,,	—
Brass	Copper+Nickel+Chromium	Va	—	0.2-0.5	5	0.5	1	1.6	3.2	34	Fine cracks	—
		Vb	—	0.2-0.5	15	0.5	1	1.8	3.6	28	,,	—
		Vc	—	0.2-0.5	25	0.5	1	1.6	3.2	34	,,	—
		Vd	—	5	5	0.5	1	1.45	2.9	26	,,	—
		Ve	—	5	15	0.5	1	1.65	3.3	33	,,	—
		Vf	—	5	25	0.5	1	1.25	2.5	29	,,	—

172

brass-nickel-chromium-plated). It is noteworthy that the brass-base samples showed no corresponding effect.

Peeling of the Composite Coating. This effect occurred on only a few (ferrous) specimens, on all of which a copper-nickel underlay had been used (group V : see Fig. 160, sample V*b*). Sample V*e* showed especially poor results, pronounced peeling being observed at a bending

Close-bend Test Piece.
Ferrous specimen No. IV, showing fine cracks in coating at bending radius of 0·55 mm.

FIG. 158.

× 3

Close-bend Test Piece.
Ferrous specimen No. VI*d*, showing severe flaking of the coating at a bending radius of 1·05 mm.

FIG. 159.

× 3

Close-bend Test Piece.
Ferrous specimen No. V*b*, showing peeling of the coating at a bending radius of 0·75 mm.

FIG. 160.

radius of 6 mm. (0·24 inch). All other types of coating withstood the close bend test without peeling away from the basis metal.

Direct comparison of these results with those obtained in parallel tests on the automobile components (Table VII) is complicated by the widely varying thickness of the latter samples. Broadly speaking, however, the experimental samples showed superior bending properties, i.e. better workability.

TABLE XXII

BALL-INDENTATION ADHESION TESTS ON EXPERIMENTAL SAMPLES

Basis Metal	Type of Coating	Mark	Brass	Copper	Nickel	Thickness of Extra Chromium Coating	Thickness of Sample, mm	Dia. of Ball, mm	Load, kg	Diameter of Impression, mm	At edge of impression	At centre of impression	Fig.
Bronze	Nickel-Chromium	IIIa	—	—	5	0·5	2·5	10	3000	6·18	Fine cracks	Fine cracks	162
		IIIb	—	—	15					6·34	" "		163
		IIIc	—	—	25					6·25	Free from cracks		—
	Nickel-Chromium	IIIa	—	—	5	0·5	2·5			5·58	Free from cracks	Free from cracks	—
		IIIb	—	—	15					5·53			—
		IIIc	—	—	25					5·58			—
Zinc-base Die Castings	Copper-Nickel-Chromium	Va	—	0·2-0·5	5	0·5	2·5			5·74	Free from cracks	Free from cracks	164
		Vb	—		15					5·59			—
		Vc	—		25					5·83			—
	Brass-Nickel-Chromium	VIa	0·2-0·5	—	5	0·5	2·5			5·57	Fine cracks	Free from cracks	165
		VIb		—	15					5·71	Free from cracks		—
		VIc		—	25					5·54			—
Aluminium Alloy Castings	Nickel-Chromium	IIIa	—	—	5	0·5	2·5			4·00	Fine cracks	Free from cracks	166
		IIIb	—	—	15					4·03	Free from cracks		—
		IIIc	—	—	25					3·93			167

174

Ball-Indentation Tests (Table XXII).

Bronze Samples. In the ball-indentation tests on the bronze samples the surface of the basis metal had become very appreciably

× 3

a	b	c
Bronze.	Zinc-base die	Aluminium alloy
	casting	casting
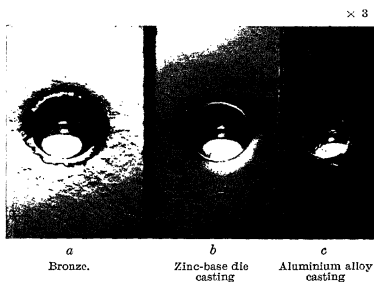
Ball-Indentation Tests.

Fig. 161.

rippled and, as a result, the chromium plating over a wide radius round the impression was rough and uneven (Fig. 161a).

Nos. IIIa and IIIb (nickel underlay 5 and 15 μ respectively) showed

× 200
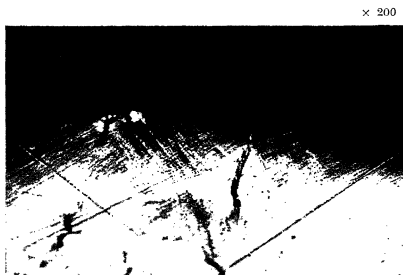
Bronze Specimen No. IIIa.
(Ni 5 μ, Cr 0·5 μ)
Cracks at intervals round edge of ball impression.

Fig. 162.

isolated cracks at the edges of the impressions (Fig. 162) : in sample IIIc, which had a nickel underlay of 25 μ, the edges of the impression were free from cracks. All the samples showed fine cracks at the centres

of the impressions ; see Fig. 163, which also shows the irregularity of the chromium surface referred to above.

The experimental bronze samples behaved very much more satisfactorily in the indentation tests than the corresponding automobile components, which had been heavily chromium-plated without an underlay, indicating that for bronze parts a thin layer of chromium over a heavy underlay of nickel gives better properties than a thick coating of chromium deposited direct on the base. No peeling or flaking of the coating occurred on any of the experimental samples of this group.

× 200
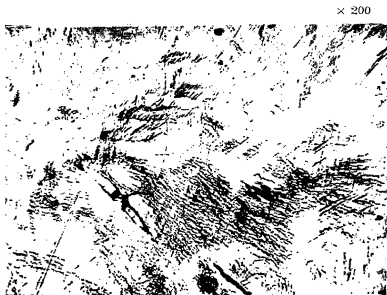
Bronze Specimen No. III*b*.
(Ni 15 *μ*, Cr 0·5 *μ*)
Cracks and rippled surface on interior of ball impression.
Fig. 163.

Zinc-base Die Castings.   On these samples the ball impression showed sharply defined edges and the surface of the chromium plating was smooth (Fig. 161*b*). With a single exception (VI*a*), all the experimental zinc-base samples remained free from cracks both at the centres and the edges of the ball impressions (Fig. 164 ; edge of V*a*).

In No. VI*a* (brass 0·2–0·5, nickel 5, chromium 0·5 *μ*), fine cracks occurred at intervals along the edge (Fig. 165) : VI*b* and VI*c*, which had thicker underlays of nickel, also showed cracks at the same position.

A comparison of the relatively slight cracking on the experimental samples, with the severely cracked condition of the corresponding automobile specimens (Table VIII : Figs. 44–47) demonstrates the beneficial effect of a thick nickel underlay.[1] No peeling or flaking of the coating was observed on any samples in this group.

[1] For a detailed discussion of the technique of nickel-plating of zinc and zinc-base alloys, see 29, 73, 136, 325, 358, 422, 443, 450, 461, 470, 473, 494, 507, 549.

× 200

Zinc-base Die Casting Specimen No. V*a*.
(Cu 0·2–0·5 µ, Ni 5 µ, Cr 0·5 µ)
Edge of ball impression, showing freedom from cracks.

FIG. 164.

× 200
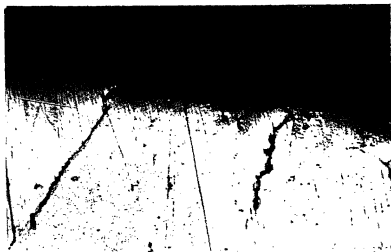
Zinc-base Die Casting Specimen No. VI*a*.
(Brass 0·2–0·5 µ, Ni 5 µ, Cr 0·5 µ)
Fine cracks at intervals round edge of ball impression.

FIG. 165.

Aluminium Alloy Castings. On these samples also the impression
was sharp and the surface of the plating showed no signs of roughening
(Fig. 161*c*). The specimens chromium-plated over a thick underlay of
nickel were free from cracks both at the centre and edge of the impres-
sions. III*a*, which had only a thin underlay of nickel, showed fine
cracks at the edge of the impression (Fig. 166). On all the aluminium-
base samples the chromium plating showed signs of " burning."

N

In the experimental samples, as in the automobile components (p. 77), adhesion of the coating bore no relation to its behaviour under

× 200

Aluminium Alloy Specimen No. IIIa.

(Ni 5 μ, Cr 0·5 μ)

Fine cracks at edge of ball impression: " burning " of chromium deposit.

FIG. 166.

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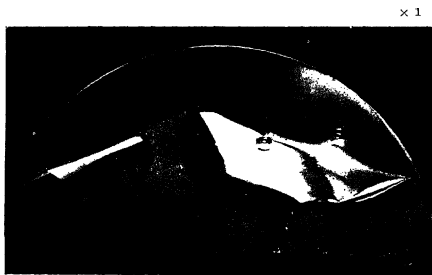
Aluminium Alloy Specimen IIIc.

(Ni 25 μ, Cr 0·5 μ)

Poor adhesion of composite coating.

FIG. 167.

ball-indentation test, e.g. IIIc (Fig. 167) peeled away easily from the base, due to poor adhesion, but no peeling or flaking occurred in the indentation tests.

Scratch-Hardness and Wear-Resistance
(Tables XXIII and XXIV)

For these tests a few directly-chromium-plated zinc-base samples were added to the specimens shown in Table XX. The chromium coatings on the additional specimens were of varying thickness, as resulting from electrodeposition treatment of 5, 10, 15 and 25 minutes respectively. Scratch-hardness and wear-resistance tests only were made on these samples.

TABLE XXIII
Scratch-Hardness of Directly-Chromium-plated Experimental Samples

Basis Metal.	Description of Test Piece.		Thickness of Chromium Coating, μ	Thickness of Sheet.		Scratch-Hardness, H.	
	Type of Coating.	Mark.		mm.	in.	Width of Scratch "S," under 3g load, μ	Reciprocal Hardness Value. $H' = \frac{1}{S}.1000$
Steel	Chromium	I	2–3	1	0·04	1·6	625
Brass	Chromium	I	2–3	1	0·04	1·3	709
Zinc-base Die Castings	Chromium	Ia	1·1	2·5	0·1	2·0	500
		Ib	1·5			1·3	709
		Ic	1·8			1·5	667
		Id	2–2·5			1·2	833

Scratch-hardness. The tests were made by the method used on the automobile components (see p. 80). In the case of specimens on which the chromium coating was only 0·5 μ thick, it proved impossible to determine the hardness accurately ; Table XXIII gives values for scratch-hardness of samples carrying a thicker coating (see also Table X). No definite relationship between thickness of chromium coating and scratch-hardness can be deduced from the values obtained, and, in view of the extent to which the hardness of electro-deposited chromium is influenced by the conditions of deposition, no regular relationship would be anticipated.

Wear-Resistance (Table XXIV). A description of the method of wear-testing is given on p. 80.

Fig. 168 shows time-to-grinding-through as a function of thickness of coating, the mean value of z = 0·75 minutes being shown for all samples having a 0·5 μ thickness of chromium.

As would be anticipated, wear-resistance rises very markedly with increase in thickness of coating, but with increasing thickness, the plating shows a growing tendency to scale off when subjected to grinding action.

TABLE XXIV

WEAR TESTS ON EXPERIMENTAL SAMPLES

Basis Metal	Description of Test Piece. Type of Coating.	Mark.	Thickness of Intermediate Layers, μ	Nickel.	Thickness of Exterior Chromium Coating, μ	Thickness of Sheet. (mm.)	(in.)	Time reqd. to grind through Chromium Coating, min.	Wear-Resistance, W. Decrease in Weight (L), per 5 mins. grinding, in mg.	Reciprocal Wear Value, W = $\frac{1}{L}$ 10000
	Chromium	I	—	—	2–3	1	0·04	15	2·0	500
	Copper-Chromium	IIa / IIb	Copper 0·2-0·5 / 5	—	0·5	1	0·04	¾–1	4·0 / 4·0	250 / 250
	Nickel-Chromium	IIIa / IIIb	—	5 / 15	0·5	1	0·04	1 / 1¼	3·0 / 2·0	333 / 500
	Nickel-Chromium (after coppering-cleaning)	IV	Cleaned in a coppering solution	15	0·5	1	0·04	1½	2·5	400
Iron or Steel	Copper-Nickel-Chromium	Va / Vb / Vc / Ve	0·2-0·5 / 5	5 / 15 / 25 / 15	0·5	1	0·04	1–1¼	4·0 / 3·5 / 3·0 / 3·0	250 / 286 / 333 / 333
	Brass-Nickel-Chromium	VIa / VIc / VIf	Brass 0·2-0·5 / 5	5 / 25 / 25	0·5	1	0·04	¾–1	4·0 / 2·5 / 3·0	250 / 400 / 333
	Nickel-Copper-Chromium	VII	Nickel 5 / Copper 5	—	0·5	1	0·04	1	4·0	250
	Nickel-Copper-Nickel-Chromium	VIII	5	15	0·5	1	0·04	¾	3·0	333
	Zinc-Brass-Nickel-Chromium	IX	Zinc 5 / Brass 5	15	0·5	1	0·04	1¼	3·5	286

Table (continued; rotated landscape table). Column headers were given on a preceding page; values below are transcribed in original row order.

Group	Alloy	Code		Copper							
	Chromium	I	—	—	—	2-3	1	0·04	22	1·5	667
Brass	Nickel-Chromium	IIIa	—	—	5	0·5	1	0·04	⅜	3·5	286
		IIIb	—	—	15				⅜	4·0	250
		IIIc	—	—	25				¾	3·0	333
	Copper-Nickel-Chromium	Va	—	Copper 0·2-0·5	5	0·5	1	0·04	⅜	4·0	250
		Vb	—		15				⅜	3·0	333
		Vc	—		25				1	3·0	333
		Vd	—	5	5				⅜	3·5	286
		Ve	—		15				¾	4·0	250
		Vf	—		25				1	3·0	333
Bronze	Nickel-Chromium	IIIa	—	—	5	0·5	2·5	0·1	⅜	4·0	250
		IIIb	—	—	15				⅜	3·0	333
		IIIc	—	—	25				¾	3·0	333
	Chromium	Ia	—	—	—	1·1	2·5	0·1	3½	2·0	500
		Ib	—	—	—	1·5			6	1·5	667
		Ic	—	—	—	1·8			18	1·5	667
		Id	—	—	—	2-2·5				1·3	769
	Nickel-Chromium	IIIa	—	—	5	0·5	2·5	0·1	⅜	4·0	250
		IIIc	—	—	25				¾	3·0	333
Zinc-base Die Castings	Copper-Nickel-Chromium	Va	—	Copper. 0·2-0·5	5	0·5	2·5	0·1	⅜	3·0	333
		Vc	—		25				¾	2·5	400
	Brass-Nickel-Chromium	VIa	Brass 0·2-0·5	—	5	0·5	2·5	0·1	⅜	2·0	333
		VIc		—	25				⅜	2·5	400
Aluminium Alloy Castings	Nickel-Chromium	IIIa	—	—	5	0·5	2·5	0·1	⅜	4·0	250
		IIIb	—	—	15				⅜	3·0	333
		IIIc	—	—	25				1	2·5	400

Fig. 169 gives the reciprocal wear values (W') for all the samples having a 0·5 μ thickness of chromium.   The results show that increase in the thickness of the nickel underlay also produces improved wear-resistance of the composite coating ; the samples carrying the thinnest underlays of nickel and those bearing an underlay of copper without nickel show the worst behaviour.   The tests on the automobile com-
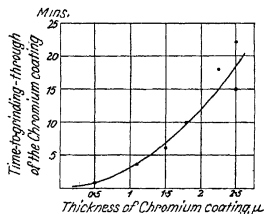
FIG. 168.—Wear-Resistance of Experimental Chromium Coatings.
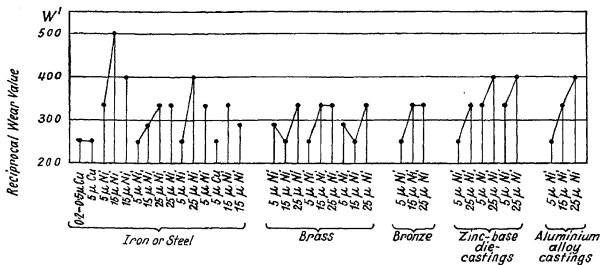
FIG. 169.—Wear-Resistance of Chromium Coatings.
Effect of Nature and Thickness of Intermediate Coatings.

ponents (see p. 85) had already indicated that hardness and wear-resistance depend to some extent on the nature of the metal used for the foundation and the underlay(s).   The effect is probably due to the considerably higher hydrogen overvoltage of copper, which favours the production of a softer and less wear-resistant chromium plating.

Resistance to Alternations of Temperature
(Table XXV)

In view of the comprehensive tests carried out on the automobile samples (see pp. 86–94), further extensive experiments were considered

unnecessary, but since the earlier tests had dealt only with specimens in which brass or bronze was the basis material (Table XII), a few additional tests were made to determine the behaviour of chromium deposited on different types of foundation. The specimens were rectangular (24 mm. × 24 mm.), and the tests, as before, consisted in repeated quenching from 300° C., in water at room temperature, until cracks appeared on the chromium plating. If no cracks occurred after 100 quenchings, the test was discontinued.

Ferrous Samples. In spite of the relatively small differences between the coefficients of thermal expansion of iron and chromium, the ferrous-base sample I showed incipient cracking after only 40 quenchings (Fig. 170). In view of the known tendency of heavy

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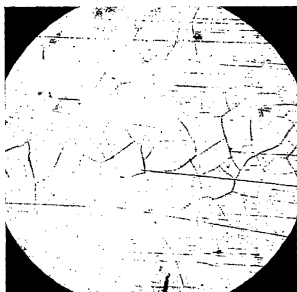
Chromium, 2–3 μ; on Steel.
Incipient cracking after 40 alternations of temperature.
Fig. 170.
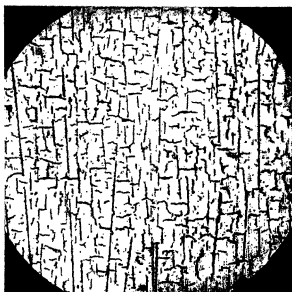
Copper, 5 μ, Chromium, 0·5 μ; on Ferrous Base.
Severe cracking after first alternation of temperature.
Fig. 171.

chromium coatings to crack, due to the presence of internal stresses, it is considered that the failure of this sample was probably attributable to the thickness of the coating (2–3 μ).

The difference between the coefficients of expansion of chromium and copper is approximately double that existing between the coefficients of chromium and iron. Samples IIb and VII, both chromium-plated over 5 μ copper, showed very pronounced cracking after only one quenching (Fig. 171), whereas IIc, which carried a thinner underlay of copper (0·2–0·5 μ), remained free from cracks.

The difference between the coefficients of chromium and of nickel is only slight. The ferrous samples chromium-plated over underlays of nickel (5–25 μ) were free from cracks. (These samples showed some flaking, presumably due to faulty adhesion.)

TABLE XXV

ALTERNATING TEMPERATURE (QUENCHING) TESTS ON EXPERIMENTAL SAMPLES

Basis Metal	Description of Test Piece. Type of Coating.	Mark	Type and Thickness of Intermediate Layers. μ	Nickel. μ	Thickness of Chromium Coating. μ	Condition of Surface.	Fig.
	Chromium	I	—	—	2–3	Incipient cracking after 40 quenchings	170
	Copper-Chromium	IIa IIb	Copper 0·2–0·5 5	— —	0·5	Free from cracks after 100 quenchings Severe cracking after the first quench	171
	Nickel-Chromium	IIIa IIIb IIIc	— — —	5 15 25	0·5	Free from cracks after 100 quenchings	—
	Nickel-Chromium (after coppering-cleaning)	IV	Cleaned in a coppering solution	15	0·5	Free from cracks after 100 quenchings	—
Iron or Steel	Copper-Nickel-Chromium	Va Vb Vc Vd Ve Vf	Copper 0·2–0·5 5	5 15 25 5 15 25	0·5	Slight peeling " " Slight peeling } Free from cracks after 100 quenchings	—
	Brass-Nickel-Chromium	VIa VIb VIc VId VIe VIf	Brass 0·2–0·5 5	5 15 25 5 15 25	0·5	— Slight peeling " " } Free from cracks after 100 quenchings	—
	Nickel-Copper-Chromium	VII	Nickel 5 Copper 5	—	0·5	Severe cracking after the first quench	—

184

Base	Coating	Code			Ni	Cr	Remarks	
Brass	Nickel-Copper-Nickel-Chromium	VIII	5	5	15	0·5	Free from cracks after 100 quenchings	—
	Zinc-Brass-Nickel-Chromium	IX	Zinc 5	Brass 5	15	0·5	Slight peeling : free from cracks after 100 quenchings	—
	Chromium	I	—	—	—	2-3	Severe cracking after the first quench : local peeling of the chromium coating	172
	Nickel-Chromium	IIIa IIIb IIIc	—	—	5 15 25	0·5	Free from cracks after 100 quenchings	—
	Copper-Nickel-Chromium	Va Vb Vc Vd Ve Vf	Copper 0·2-0·5	5	5 15 25 5 15 25	0·5	Free from cracks after 100 quenchings	—
Bronze	Nickel-Chromium	IIIa IIIb IIIc	—	—	5 15 25	0·5	Free from cracks after 100 quenchings	—
Zinc-base Die Castings	Nickel-Chromium	IIIa IIIb IIIc	—	—	5 15 25	0·5	Free from cracks after 100 quenchings	—
	Copper-Nickel-Chromium	Va Vb Vc	0·2-0·5	—	5 15 25	0·5	Free from cracks after 100 quenchings	—
	Brass-Nickel-Chromium	VIa VIb VIc	Brass 0·2-0·5	—	5 15 25	0·5	Free from cracks after 100 quenchings	—
Aluminium Alloy Castings	Nickel-Chromium	IIIa IIIb IIIc	—	—	5 15 25	0·5	Peeling of the chromium coating ; Free from cracks after 100 quenchings	—

Brass Samples. The widest difference in coefficient of thermal expansion occurring in the metals under consideration is that between brass and chromium. As would be anticipated from this fact, the directly-chromium-plated brass sample I showed pronounced cracking
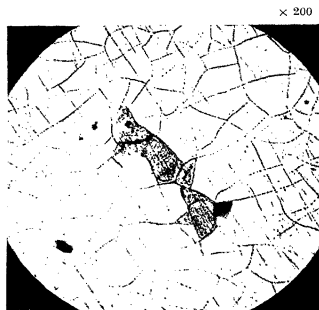
Chromium, 2–3 μ; on Brass.
Severe cracking after one alternation of temperature. Local peeling of the chromium coating.
FIG. 172.

after the first quenching (Fig. 172). In this case also the chromium coating was a thick one (2–3 μ), but on a ferrous base the same type of plating withstood 40 quenchings before cracking, thus clearly indicating the influence of the basis metal. All the other brass samples, which were chromium-plated over a nickel underlay, remained free from cracks.

TABLE XXVI

DIFFERENCES IN THERMAL COEFFICIENT OF EXPANSION BETWEEN CHROMIUM AND THE METALS AND ALLOYS IN IMMEDIATE CONTACT WITH THE CHROMIUM COATINGS *

	Coefficient of Thermal Expansion. $\times 10^{-8}$ mm.^{8}		Difference. $\times 10^{-8}$, mm.
Chromium 840	Iron	1260	420
	Brass	1982	1142
	Bronze	1820	980
	Copper	1650	810
	Nickel	1300	460

* See note on values for coefficients of thermal expansion given at foot of Table XI, p. 87.

Bronze Samples. The directly-chromium-plated automobile speci-

mens showed cracks after 50 quenchings ; on the experimental samples, coated with an underlay of nickel, no cracks were observed.

Zinc- and Aluminium-Alloy Samples. The experimental samples, in both cases chromium-plated over an underlay of nickel, also remained free from cracks.

As in the earlier series of tests, the behaviour of the chromium coatings under reversals of temperature was found to be determined mainly by the differences between the coefficients of thermal expansion of chromium and of the metals used as underlays. The beneficial influence of an underlay of a metal whose coefficient is closely similar to that of chromium, viz. nickel, is clearly demonstrated by this series of tests.[1] The thickness of the chromium coating is also an important factor in determining its reaction to conditions of rapid temperature change.

Potential Measurements (Table XXVII)

Potential measurements were made on all the experimental samples, against the normal calomel electrode, in 1 per cent. sodium chloride solution, after one, two, five and twenty-five days. (See also p. 97, dealing with parallel tests on automobile parts.)

The ferrous-base samples showed widely divergent potentials ; in some cases the values were close to those of the uncoated steel, in others they were considerably higher. The presumption is that in the former case the coatings were extremely porous and in the latter, sound and compact. A noteworthy feature is the rise in potential which accompanies increased thickness of nickel underlay.

[1] In this connection Birett [429] makes the following observations : " A point which is almost entirely overlooked is the question of coefficient of thermal expansion. The metals of the coating must necessarily take part in all the volume changes occurring in the basis material, so that at first sight it appears to be immaterial whether large differences exist between the coefficients of expansion of the basis metal and that of the coating, since the elastic limit of the deposit can never be exceeded. In practice, however, it has been demonstrated that volume changes which accompany repeated changes in temperature, even if the changes are small, sometimes produce disturbances, and that the smaller the differences between the coefficients of thermal expansion of the basis metal and that of the coating, the better do the plated parts behave under such conditions. The disturbance so produced may be compared to the well-known fatigue phenomena occurring in the endurance testing of metals and alloys. This question has assumed a very practical significance in connection with the electrodeposition of chromium, where the use of underlay coatings has been adopted to overcome certain difficulties. In this connection it may be of interest to mention that the use of interlays of materials of intermediate coefficient of thermal expansion has been successfully adopted in the paint industry, and has, to a large extent, overcome difficulties arising from excessive difference between the elasticity of the ground coats and the outer coats." The present authors associate themselves *in toto* with the above remarks. (See also 111.)

TABLE XXVII

POTENTIAL MEASUREMENTS ON EXPERIMENTAL SAMPLES (1 PER CENT. SODIUM CHLORIDE SOLUTION : ROOM TEMPERATURE)

Basis Metal	Description of Test Piece — Type of Coating	Mark	Thickness of Intermediate Layers, μ	Nickel	Thickness of Exterior Chromium Coating, μ	Potential against Normal Calomel Electrode, volts, after — 1 day	2 days	5 days	25 days
Iron or Steel	Chromium	I	—	—	2–3	− 0·55	− 0·58	− 0·58	− 0·65
	Copper-Chromium	IIa	Copper. 0·2–0·5	—	0·5	− 0·56	− 0·56	− 0·61	− 0·64
		IIb	5	—		− 0·35	− 0·51	− 0·57	− 0·63
	Nickel-Chromium	IIIa	—	5	0·5	− 0·61	− 0·55	− 0·58	− 0·65
		IIIb	—	15		− 0·31	− 0·29	− 0·38	− 0·45
	Nickel-Chromium (after copper-ing cleaning)	IV	Cleaned in a copper-ing bath	15	0·5	− 0·33	− 0·38	− 0·37	− 0·48
	Copper-Nickel-Chromium	Va	0·2–0·5	5	0·5	− 0·29	− 0·36	− 0·49	− 0·63
		Vb		15		− 0·29	− 0·33	− 0·50	− 0·54
		Vc	5	25		− 0·32	− 0·34	− 0·41	− 0·38
		Ve		15		− 0·33	− 0·33	− 0·35	− 0·36
	Brass-Nickel-Chromium	VIa	Brass 0·2–0·5	5	0·5	− 0·31	− 0·36	− 0·42	− 0·45
		VIc		25		− 0·27	− 0·31	− 0·33	− 0·35
		VIf	5	25		− 0·25	− 0·30	− 0·28	− 0·34
	Nickel-Copper-Chromium	VII	Copper 5 / Nickel 5	—	0·5	− 0·43	− 0·45	− 0·48	− 0·52
	Nickel-Copper-Nickel-Chromium	VIII	5	15	0·5	− 0·42	− 0·45	− 0·50	− 0·57
	Zinc-Brass-Nickel-Chromium	IX	Brass 5 / Zinc 5	15	0·5	− 0·28	− 0·29	− 0·32	− 0·45

Base	Coating	Spec.	I	Copper / Brass	Thickness	2–3	−0·18	−0·18	−0·21	−0·22
Brass	Chromium	—	—	—	—	—	—	—	—	—
	Nickel-Chromium	IIIa	—	—	5	0·5	−0·32	−0·37	−0·33	−0·33
		IIIb	—	—	15		−0·24	−0·23	−0·18	−0·17
		IIIc	—	—	25		−0·22	−0·20	−0·17	−0·12
	Copper-Nickel-Chromium	Va	—	Copper 0·2–0·5	5	0·5	−0·18	−0·13	−0·08	−0·10
		Vb			15		−0·19	−0·13	−0·12	−0·13
		Vc			25		−0·20	−0·22	−0·18	−0·11
		Vd		5	5		−0·19	−0·14	−0·13	−0·12
		Ve			15		−0·23	−0·17	−0·12	−0·12
		Vf			25		−0·20	−0·25	−0·22	−0·16
Bronze	Nickel-Chromium	IIIa	—	—	5	0·5	−0·17	−0·13	−0·15	−0·16
		IIIb			15		−0·14	−0·16	−0·13	−0·18
		IIIc			25		−0·16	−0·12	−0·13	−0·13
	Chromium	La	—	—	—	1·1	−0·97	−0·97	−0·98	−1·01
		Lb				1·5	−0·96	−0·98	−0·97	−0·98
		Lc				1·8	−0·97	−1·00	−1·02	−1·01
		Ld				2–2·5	−0·95	−0·96	−0·97	−1·00
Zinc-base Die-Castings	Nickel-Chromium	IIIa	—	—	5	0·5	−0·94	−0·08	−0·98	−0·97
		IIIc			25		−0·40	−0·43	−0·96	−0·98
	Copper-Nickel-Chromium	Va	—	Copper 0·2–0·5	5	0·5	−0·41	−0·40	−0·97	−1·03
		Vc			25		−0·35	−0·31	−0·50	−0·98
	Brass-Nickel-Chromium	VIa	—	Brass 0·2–0·5	5	0·5	−0·89	−0·99	−1·02	−1·01
		VIc			25		−0·31	−0·32	−0·45	−0·96
Aluminium Alloy Castings	Nickel-Chromium	IIIa	—	—	5	0·5	−0·68	−0·67	−0·68	−0·71
		IIIb			15		−0·38	−0·41	−0·42	−0·69
		IIIc			25		−0·28	−0·35	−0·51	−0·68

The brass- and bronze-base experimental samples, like the corres-
ponding automobile specimens (see p. 99) showed varying values, some
closely similar to that of chromium, some approximating to that of the
underlay and some to that of the basis metal. The results confirm
that with the types of basis metal used, potential measurements give
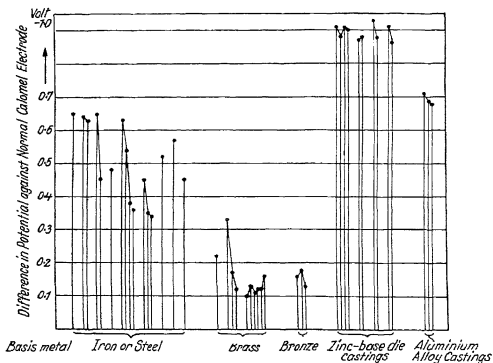
Fig. 173.—Potential Measurements on Experimental Samples.
(Readings after 25 days in 1 per cent. sodium chloride solution.)

no reliable indication of the degree of protection afforded by the coating,
nor of its porosity.

The zinc- and aluminium-base samples all showed potentials approxi-
mating to the somewhat low values of the respective alloys in the un-
coated condition (Table XIII). The results are in agreement with
those obtained in the earlier tests.

Porosity Tests (Table XXVIII)

For the ferrous-, brass- and bronze-base samples, the methods of
test used were identical with those employed in the earlier tests (p. 115).
The zinc-base samples were tested by two methods, viz. immersion in
copper sulphate solution (for details of this method see p. 110) and by
treatment with a strongly alkaline hot solution of sugar (p. 110). As
in the earlier tests, the aluminium alloy specimens were treated with
a gelatin solution containing 2·5 per cent. sodium hydroxide, applied
by pouring over the specimen. (The values shown in Table XXVIII
for "no. of pores per sq. cm." are the averages of at least five
measurements for each specimen.)

TABLE XXVIII

Porosity Tests on Experimental Samples

Basis Metal	Description of Test Piece — Type of Coating	Mark	Thickness of Intermediate Layers, μ	Nickel	Thickness of Exterior Chromium Coating, μ	No. of Pores per sq. cm. (average)
Iron or Steel	Chromium	I	—	—	2·3	15
	Copper-Chromium	IIa	Copper 0·2–0·5	—	} 0·5	40
		IIb	5	—		30
	Nickel-Chromium	IIIa	—	5	} 0·5	30
		IIIb	—	15		12
		IIIc	—	25		8
	Nickel-Chromium (after coppering-cleaning)	IV	Cleaned in coppering solution	15	0·5	12
	Copper-Nickel-Chromium	Va	} 0·2–0·5	5		20
		Vb		15		5
		Vc		25	} 0·5	0·5
		Vd	} 5	5		25
		Ve		15		8
		Vf		25		2
	Brass-Nickel-Chromium	VIa	Brass } 0·2–0·5	5		22
		VIb		15		7
		VIc		25	} 0·5	1·5
		VId	} 5	5		14
		VIe		15		3·5
		VIf		25		0·25
	Nickel-Copper-Chromium	VII	Nickel 5	Copper 5	0·5	4
	Nickel-Copper-Nickel-Chromium	VIII	5	5	15 — 0·5	3
	Zinc-Brass-Nickel-Chromium	IX	Zinc 5	Brass 5	15 — 0·5	6
Brass	Chromium	I	—	—	2·3	20
	Nickel-Chromium	IIIa	—	Nickel 5	} 0·5	21
		IIIb	—	15		8
		IIIc	—	25		6
	Copper-Nickel-Chromium	Va	} 0·2–0·5	Copper 5		22
		Vb		15		12
		Vc		25	} 0·5	1
		Vd	} 5	5		12
		Ve		15		18
		Vf		25		6·5
Bronze	Nickel-Chromium	IIIa	—	5	} 0·5	8
		IIIb	—	15		8
		IIIc	—	25		1·5
Zinc-base Die Castings	Nickel-Chromium	IIIa	—	5	} 0·5	18
		IIIb	—	15		8
		IIIc	—	25		3
	Copper-Nickel-Chromium	Va	} 0·2–0·5	5	} 0·5	20
		Vb		15		11
		Vc		25		1·5
	Brass-Nickel-Chromium	VIa	Brass } 0·2–0·5	5	} 0·5	17
		VIb		15		10
		VIc		25		2·5
Aluminium Alloy Castings	Nickel-Chromium	IIIa	—	5	} 0·5	26
		IIIb	—	15		8
		IIIc	—	25		4

In view of the many representative photographs contained in the
section dealing with porosity tests on automobile parts (Figs. 62–105)
it was considered unnecessary to give a further complete series of illus-

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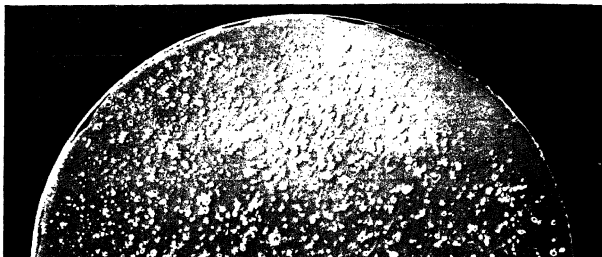
Nickel-chromium Coating, on Aluminium Alloy Casting.
(Specimen IIIa : Ni 5 μ, Cr 0·5 μ.)
26 pores per sq. cm.
Showing hydrogen bubbles in gelatin film.
FIG. 174.

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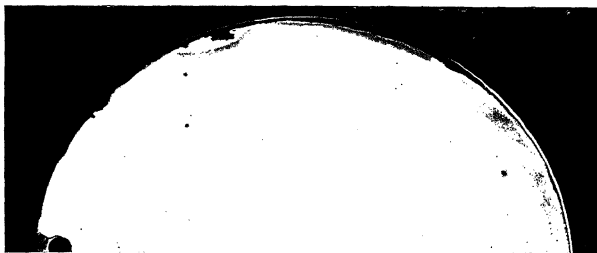
Nickel-chromium Coating, on Aluminium Alloy Casting.
(Specimen IIIc : Ni 25 μ, Cr 0·5 μ.)
4 pores per sq. cm.
Showing hydrogen bubbles in gelatin film.
FIG. 175.

trations relating to the experimental samples. Two photographs of
chromium-plated aluminium-alloy castings are, however, reproduced as
being specially characteristic of the clarity of delineation of the hydrogen
bubbles left adhering to the gelatin film, and as illustrating the ease

with which the number of pores may be counted over any given surface area.

Fig. 174 shows sample IIIa (nickel underlay 5 μ) which had a rating of 26 pores per sq. cm., as compared with IIIc (nickel 25 μ : Fig. 175), for which the count was only 4 pores.   In Fig. 176 number-of-
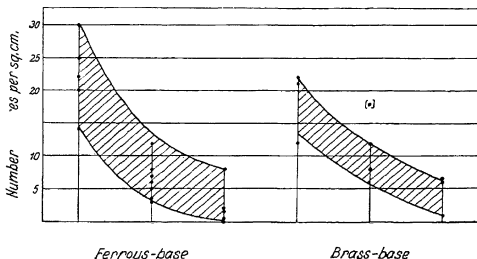
FIG. 176.—Porosity Rating as a Function of Thickness of Nickel Underlay.
(Experimental Ferrous- and Brass-base Samples.)

pores-per-sq.-cm., for ferrous- and brass-base samples, is plotted as a function of thickness of nickel underlay, without reference to any other additional interlay(s).   The graph should be compared with the corresponding curves relating to the automobile parts (Figs. 102 and 103).

In the case of the automobile parts, the fact that very few of the samples carried a nickel underlay of 15 μ or above precluded the establishment of a conclusive relationship between thickness of nickel underlay and degree of porosity.   The graphs relating to the experimental samples, however, indicate very clearly the beneficial effect of a thick layer of nickel.

Fig. 177 summarises all the values given in Table 28.

The results of the porosity tests lead to the following conclusions :

1. Thick chromium plating (2–3 μ), used alone, affords no guarantee of freedom from porosity [191, 331].

2. Samples plated with a copper underlay only also show high porosity.

3. In all cases, whatever the basis material, a 5 μ underlay of nickel is inadequate ; a minimum of 15 μ is required to produce any marked decrease in porosity and the improvement is much enhanced by increasing the thickness to 25 μ [191, 331].

4. The presence of an interlay of copper or brass in addition to the nickel underlay appears to have no substantial effect on porosity (see also p. 221).
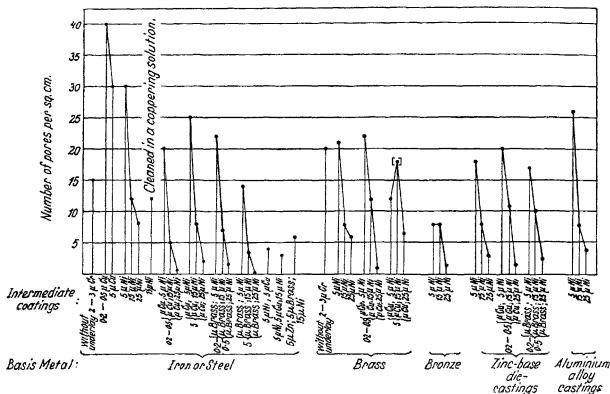
FIG. 177.—Porosity Ratings of Experimental Samples.

Corrosion Tests

The strikingly regular decrease in " no. of pores per sq. cm." observed with progressive increase in thickness of nickel underlay (Table XXVIII : Fig. 177) had already demonstrated the existence of an intimate relationship between thickness of nickel underlay and resistance to corrosion. Additional confirmatory tests were made on the ferrous-base samples listed in Table XXIX. The specimens were cleaned with alcohol and ether, dried, weighed, and placed in upright vessels each containing 2000 c.c. of sea-water. Evaporation during test was compensated by the addition of distilled water. The specimens were kept in the solution for forty-two weeks, in the course of which period they became covered with a flocculent brown coating of rust ; this film was in most cases only lightly adherent. At the end of the forty-two-week period, the specimens were cleaned, dried and re-weighed. The results of the tests show close agreement with those of the porosity tests. Samples IIa and IIb, chromium-plated over an underlay of copper, which showed the highest number of pores, also suffered the greatest loss in weight in the corrosion tests. In all the other samples, on which the chromium had been deposited over an underlay of nickel, there is a gradual and consistent *increase* in corrosion-resistance (decrease in loss of weight) with *increase* in thickness of nickel underlay.

In order to correlate the results of the second group of tests with

TABLE XXIX

ARTIFICIAL SEA-WATER CORROSION TESTS ON EXPERIMENTAL SAMPLES
(Duration of Test : 42 weeks)

Basis Metal.	Description of Test Piece		Thickness of Intermediate Layers, μ			Thickness of Exterior Chromium Coating, μ	Dimensions of Sample.	Loss in Weight, $g.$
	Type of Coating.	Mark.	Brass.	Copper.	Nickel.			
Steel	Copper-Chromium	IIa IIb	—	0·2–0·5 5	—	} 0·5	100 × 150 mm. (4 × 6 in.)	3·5505 2·5964
	Nickel-Chromium	IIIa IIIb IIIc	—	—	5 15 25	} 0·5		1·6125 1·0946 0·9788
	Copper-Nickel-Chromium	Va Vb Vc	—	}0·2–0·5	5 15 25	} 0·5		1·2919 1·2148 1·1049
		Vd Ve Vf	—	} 5	5 15 25	} 0·5		1·2748 1·1831 0·8500
	Brass-Nickel-Chromium	VIa VIb VIc	}0·2–0·5	—	5 15 25	} 0·5		1·8201 1·2913 1·0411
		VId VIe VIf	} 5	—	5 15 25	} 0·5		1·6575 1·1858 0·9982
	Nickel-Copper-Chromium	VII	Nickel 5	Copper 5	—	0·5		2·0984
	Nickel-Copper-Nickel-Chromium	VIII	5	5	15	0·5		1·3547

those of the earlier series, a general rating (G) was calculated on the basis described on p. 132. Since the primary object of these tests was to confirm the effect of varying thickness of nickel underlay on the life of the chromium coating, the tests were continued only long enough to establish a definite relationship between the two factors (forty-two weeks). A summary of the results is given in Table XXX and Fig. 179.

Atmospheric Exposure (Weathering Tests).[1] Fig. 180 shows ferrous sample I, directly chromium-plated (2–3 μ), after forty-two weeks' exposure ; the specimen had a porosity rating of 15. After only two weeks, considerable flaking was observed over the entire surface.[2]

[1] The specimens were exposed on the roof of the Staatliches Materialprüfungs-samt, Berlin-Dahlem, from March 15, 1932, until January 1, 1933.

[2] In the A.E.S.—A.S.T.M.—N.B.S. tests [485] directly-chromium-plated samples (0·0002 inch : 0·005 mm.) are reported to have " rusted badly in all locations and to be too poor to warrant consideration for outdoor exposure."
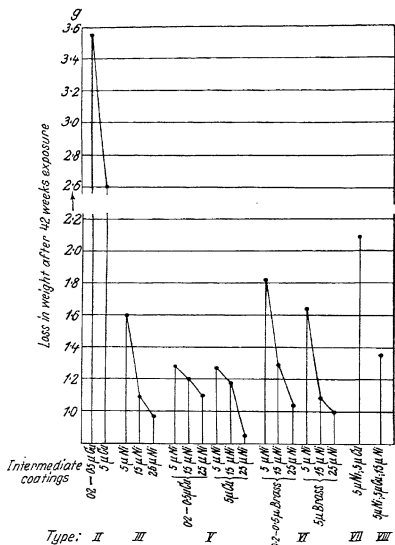
FIG. 178.—Sea-Water Immersion Tests.

Influence of Increasing Thickness of Nickel Underlay on Corrosion-Resistance of Chromium Plating on Steel.
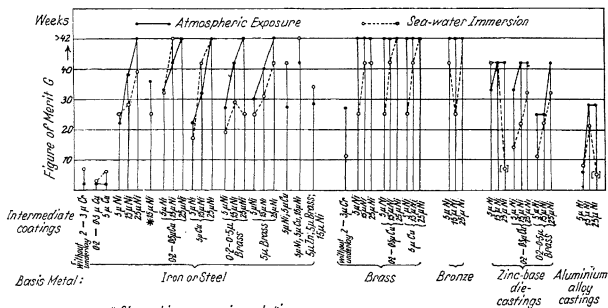
FIG. 179.—Corrosion Tests on Experimental Samples. Summary of Results.

× 1

Atmospheric Exposure Test.

Chromium Coating, on Ferrous Base.

(Cr 2-3 μ.)

15 pores per sq. cm.; G = 2 weeks.

Showing almost complete disintegration of chromium coating after 42 weeks' exposure

FIG. 180.

TABLE XXX

SUMMARY OF CORROSION TESTS ON EXPERIMENTAL SAMPLES

Basis Metal	Description of Test Piece — Type of Coating	Mark	Thickness of Intermediate Layers, μ — Brass	Copper	Nickel	Thickness of Exterior Chromium Coating, μ	No. of Weeks required to produce γ-type attack — Atmospheric Tests	Fig.	Sea Water Immersion Tests	Fig. of Merit, t. — Fig.
Iron or Steel	Chromium	I	—	—	Nickel.	2-3	2	180	7	—
	Copper-Chromium	IIa	—	0·2-0·5	—	0·5	2	—	3	184
		IIb	—	5	—		2	—	6	—
	Nickel-Chromium	IIIa	—	—	5	0·5	22	—	25	—
		IIIb	—	—	15		38	—	28	—
		IIIc	—	—	25		> 42	—	39	—
	Nickel-Chromium (after coppering-cleaning)	IV	—	Cleaned in a coppering solution	15	0·5	36	—	25	—
	Copper-Nickel-Chromium	Va	—	0·2-0·5	5	0·5	33	—	32	—
		Vb	—		15		42	—	42	—
		Vc	—		25		> 42	—	> 42	—
		Vd	—	5	5		22	—	17	—
		Ve	—		15		32	—	42	—
		Vf	—		25		> 42	—	42	—
	Brass-Nickel-Chromium	VIa	0·2-0·5	—	5	0·5	27	—	19	—
		VIb		—	15		42	—	29	—
		VIc		—	25		> 42	—	25	—
		VId	5	—	5		30	—	25	—
		VIe		—	15		40	—	31	—
		VIf		—	25		> 42	—	42	185
	Nickel-Copper-Chromium	VII	Nickel 5	Copper 5	—	0·5	27	181	42	—

198

Basis metal	Coating system	Clause								
	Nickel-Copper-Nickel-Chromium	VIII	Zinc 5	Brass 5	15	0·5	42	—	34	—
	Zinc-Brass-Nickel-Chromium	IX	—	—	15	0·5	28	—	11	186
	Chromium	I	—	—	—	2–3	27	—		187
Brass	Nickel-Chromium	IIIa	—	—	5	⎫	>42	—	25	188
		IIIb	—	—	15	0·5	>42	182	42	—
		IIIc	—	—	25	⎭	>42	—	42	—
	Copper-Nickel-Chromium	Va	—	Copper	5	⎫	>42	—	25	—
		Vb	⎱0·2–0·5		15		>42	—	42	—
		Vc		5	25	0·5	>42	—	42	—
		Vd			5		>42	—	25	—
		Ve			15		>42	—	42	—
		Vf			25	⎭	>42	—	42	—
Bronze	Nickel-Chromium	IIIa	—	—	5	⎫	>42	—	42	—
		IIIb	—	—	15	0·5	>42	—	25	—
		IIIc	—	—	25	⎭	>42	—	42	—
Zinc-base Die Castings	Nickel-Chromium	IIIa	—	—	5	⎫	33	—	42	—
		IIIb	—	—	15	0·5	42	—	42	—
		IIIc	—	—	25	⎭	42	—	(7)	—
	Copper-Nickel-Chromium	Va	—	Copper	5	⎫	33	—	14	—
		Vb		⎱0·2–0·5	15	0·5	42	—	22	—
		Vc			25	⎭	42	—	32	—
	Brass-Nickel-Chromium	VIIa	Brass		5	⎫	25	—	11	189
		VIIb	⎱0·2–0·5		15	0·5	25	183	22	—
		VIIc			25	⎭	42	—	32	—
Aluminium Alloy Castings	Nickel-Chromium	IIIa	—	—	5	⎫	6	—	8	190
		IIIb	—	—	15	0·5	28	—	21	—
		IIIc	—	—	25	⎭	28	—	(5)	—

× 1

Atmospheric Exposure Test.

Nickel-copper-chromium Coating, on Ferrous Base.

(Ni 5 μ, Cu 5 μ, Cr 0·5 μ.)

4 pores per sq. cm.: G = 27 weeks.
Flaking at irregular intervals over the entire surface.

FIG. 181.

Atmospheric Exposure Test.

Nickel-chromium coating, on Brass.

(Ni 25 μ, Cr 0·5 μ.)

6 pores per sq. cm.; G = 42 weeks.

Free from flaking or peeling of the coating.

FIG. 182.

Fig. 181 shows a ferrous sample of type V (nickel 5, copper 5, chromium 0·5 μ) : porosity rating 4 : G = 27 weeks. Flaking occurred at irregular intervals over the whole surface.

Fig. 182 is a representative brass sample (IIIc : nickel 25, chromium 0·5 μ : porosity rating 6). At the end of the full forty-two-week period no flaking or peeling of the coating had occurred.

Fig. 183 shows aluminium alloy sample IIIa, coated with nickel 5, chromium 0·5 μ : porosity rating 26. During exposure, the sample

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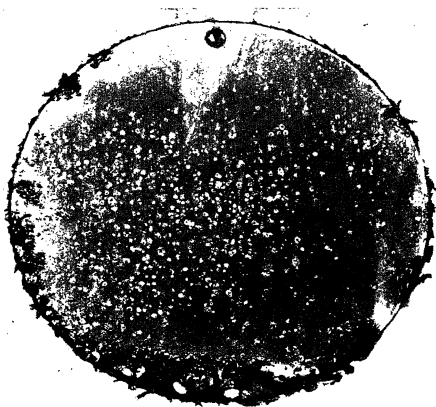
Atmospheric Exposure Test.
Nickel-chromium coating, on Aluminium Alloy Casting.
(Ni 5 μ ; Cr 0·5 μ.)
26 pores per sq. cm. : G = 6 weeks.
Slight flaking at centre : blistering and severe peeling at edges.
FIG. 183.

became coated with a dirty grey deposit, underneath which, at the centre, numerous small patches of flaking were observed. At the edges some blisters had formed and severe peeling of the chromium coating was observed.

Sea-Water Immersion Tests (Table XXX). The ferrous sample of type IIa (copper 0·2–0·5, chromium 0·5 μ), whose porosity rating was about 40, was coated after only three weeks' exposure with a brown film of rust. Under the rust deposit the coating flaked off at several points (G = 3) ; see Fig. 184.

Sea-Water Immersion Test.

Copper-chromium Coating, on Ferrous
(Cu 0·2–0·5 μ, Cr 0·5 μ.)

40 pores per sq. cm.: G = 3 weeks.
Heavily rusted: widespread flaking.

FIG. 184.

Fig. 185 shows ferrous sample VI*f*, carrying a thick nickel underlay (brass 5, nickel 25, chromium 0·5 μ) after 42 weeks (G = 42). The porosity rating of this specimen was only 0·25. No flaking or peeling of the coating had occurred, but the surface showed numerous small blisters, indicative of the fact that moisture had penetrated through the fine pores to the basis metal and had there produced progressive rusting. Had the exposure test been of longer duration the gradual growth of the layer of rust would eventually have burst the blisters and resulted in peeling of the chromium plating. On samples carrying thinner underlays of nickel, the blisters in some cases formed after shorter periods of exposure. Fig. 186 shows a typical example.

The brass sample of type I (2–3 μ chromium without underlay) showed specially poor results (porosity rating 20 : G = 11) ; peeling was observed over a considerable portion of the surface (Fig. 187). All the other brass samples, which had been chromium-plated over an underlay, gave considerably longer life and showed appreciably less deterioration of the chromium coating. Fig. 188 shows a typical specimen.

On the zinc-base samples, a whitish coating of zinc salts formed and gradually spread over the whole surface ; in the majority of cases the deposit was easily removable. Fig. 189 shows VI*a* (brass 0·2–0·5, nickel 5, chromium 0·5 μ : porosity rating 17 : G = 11), after removal of the white surface deposit. Flaking and peeling was observed at irregular intervals over the whole surface, but in the regions where the chromium plating had remained free from attack, it was clear and bright.

The results obtained on the aluminium-base samples were similar to those on the zinc-base specimens, but in the former case the dirty grey surface deposit adhered more firmly than the whitish coating formed on the zinc-base specimens. Fig. 190 shows a typical specimen before removal of the deposit. Flaking and peeling had occurred under the film of corrosion product.

Sea-Water Spray Tests. The results confirmed the conclusions drawn from the tests on the automobile components, viz. that sea-water spray constitutes a severe test for coatings deposited on base metal foundations, e.g. iron, aluminium, zinc.

Figs. 191 and 192 show aluminium-base samples III*a* and III*c*, carrying, respectively, nickel 5, chromium 0·5 μ (porosity rating 26) and nickel 25, chromium 0·5 μ (porosity rating 4) ; both are shown after one hundred days' exposure. Indications of γ-type corrosion were observed after eight and thirteen days respectively, but the specimens were left in the spray in order that the course of the subsequent corrosion attack and deterioration might be observed. Sample III*a* became covered over almost the whole surface with a dirty grey coating of aluminium salts (Fig. 191 : see also Fig. 174). Underneath the

Sea-Water Immersion Test.

Brass-nickel-chromium Coating, on Ferrous Base.

(Brass 5 μ, Ni 25 μ, Cr 0·5 μ.)

0·25 pore per sq. cm. : G = 42 weeks.

Blistered, but free from flaking or peeling of the coating.

FIG. 185.

Sea-Water Immersion Test.

Zinc-brass-nickel-chromium Coating, on Ferrous Base.

(Zn 5 μ, Brass 5 μ, Ni 15 μ, Cr 0·5 μ.)

6 pores per sq. cm. : G = 34 weeks.
Patches of severe rusting, accompanied by peeling of the coating.

FIG. 186.

Sea-Water Immersion Tests.

Chromium Coating, on Brass.

(Cr 2–3 μ.)

20 pores per sq. cm.; G = 11 weeks.

Widespread peeling of the coating.

FIG. 187.

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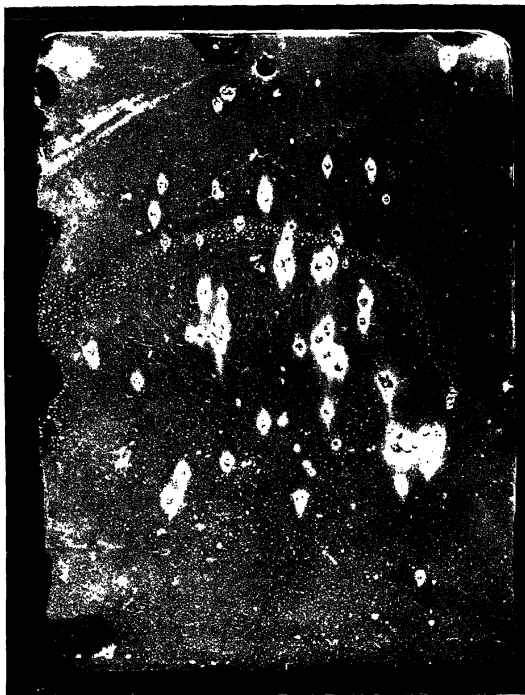
Sea-Water Immersion Test.

Nickel-chromium Coating, on Brass.

(Ni 5 μ, Cr 0·5 μ.)

21 pores per sq. cm. : $G = 25$ weeks.
Blistering and incipient flaking of the coating.

FIG. 188.

Sea-Water Immersion Test.
Nickel-chromium Coating, on Aluminium Alloy Casting.
(Ni 5 μ, Cr 0·5 μ.)
28 pores per sq. cm.; G = 8 weeks.
Dirty grey adherent film of corrosion product: flaking and peeling of the chromium coating.

FIG. 190.
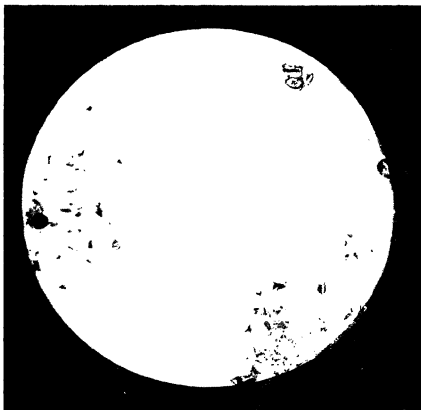
Sea-Water Immersion Test.
Brass-nickel-chromium Coating, on Zinc-base Die Casting.
(Brass 0·2–0·5 μ, Ni 5 μ, Cr 0·5 μ.)
17 pores per sq. cm.; G = 11 weeks.
Condition of coating after removal of film of corrosion product, showing flaking at irregular intervals.

FIG. 189.

Sea-Water Spray Test.

Nickel-chromium Coatings on Aluminium Alloy Castings.

(IIIa : Ni 5 μ, Cr 0·5 μ)   (IIIc : Ni 2·5 μ, Cr 0·5 μ)
26 pores per sq. cm.   4 pores per sq. cm.

Fig. 191.   Fig. 192.

coating of corrosion product the chromium coating had flaked and peeled away over small areas. Sample IIIc showed only a small amount of corrosion product (Fig. 192), but pronounced scaling had occurred and the coating had swollen. Due to the very much smaller number of pores, the corrosion of the basis metal had taken place mainly *under* the plating, and the gradually increasing volume of corrosion product had burst the thick coating over large areas, forcing it away from the base. The indication is that the number of pores has an important bearing on the *type* of deterioration undergone by the exterior coating [cf. 485].

It may be noted that whereas in the earlier series of corrosion tests the behaviour of the ferrous-base specimens was less satisfactory in the atmospheric than in the sea-water tests, the results in the second series are reversed. Attention has already been directed, however, to the numerous variables affecting the results of atmospheric tests ; direct comparison of the two series of results is not possible.

The results of the second series of tests provide convincing proof of the influence of the nickel underlay on the life of the coating under corrosive attack. The thicker the layer of nickel, the fewer the pores penetrating through to the basis metal, the greater the resistance to corrosion, and the longer the life of the coated part (see Fig. 179 and Table XXX). The findings of Baker [90, 191] are in line with this conclusion, and confirmatory results have also been obtained in the A.E.S.—A.S.T.M.—N.B.S. tests (also 134, 398). The value of thick coatings on zinc-base alloys under atmospheric exposure is also demonstrated by tests reported by Anderson [478].

Tests on Greased Specimens. The tests described below were made with the object of investigating the possibility of blocking the pores of the chromium coating with vaseline, or grease mixtures, to such an extent as to prevent access of moisture to the underlying metal.

Four sections of the ferrous sample El (copper 0·4, nickel 1·5, chromium 0·4 μ), showing a porosity rating of 14, and a very short life in the corrosion tests (G = 2 : Fig. 111) were exposed in the following conditions to the action of sea water :

  1. Without greasing.
  2. Smeared with vaseline.
  3 and 4. Smeared with commercial automobile grease.

After twenty weeks' exposure the following observations were made :
  1. Showed heavy rusting and clearly defined flaking of the chromium coating (Fig. 193).

2. Showed only a rusty graining effect.

3 and 4. Had remained completely unattacked (Fig. 193).

The results indicate that blocking the pores with greasy substances confers good protection against corrosion. Such protection is only temporary, however, since grease-containing mixtures gradually oxidise under the action of moisture and oxygen and the resulting decomposition terminates their protective power. Greasing can be recommended for vehicles standing unused for periods, provided that moisture which deposits during variations in temperature is not dried or wiped off.

× 1
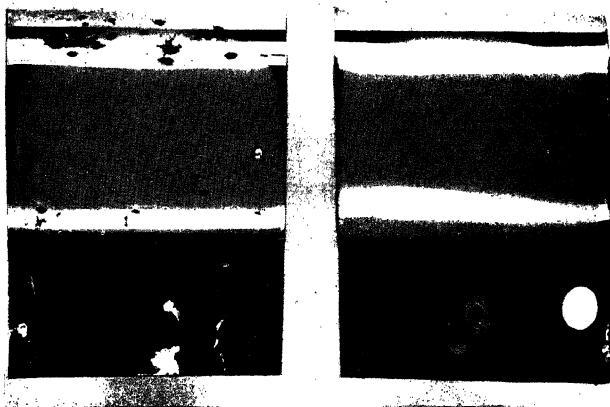
Sea-Water Test on Greased and Ungreased Samples.

No. 4: E 1 (Cu 0·4 μ, Ni 1·5 μ, Cr 0·4 μ; on Ferrous Base.)

I   II
Ungreased   Greased
Condition of surface after 20 weeks' exposure to sea-water.
FIG. 193.

CHAPTER XII

SUMMARY OF INVESTIGATION [1]

The results of the tests made on the automobile parts and the experimental samples may be summarised from three points of view :
1. Properties required in Metal Coatings for Automobile Parts.
2. Methods of Test.
3. Data obtained from the Two Series of Tests.

External Appearance. In addition to their other uses, metal coatings fulfil a pre-eminently decorative function. They should therefore be characterised by a pleasing colour and lustre and be free from surface defects (stains, blisters and other excrescences, cracks, flakes, etc.).

Visual examination is, as a rule, an adequate means of determining surface quality, but in special cases investigation of other properties, e.g. reflectivity, may be desirable. For the detection of minute surface defects (fine cracks and pores in the coating) microscopic examination is essential.

The automobile parts received for examination very clearly indicate the existing preference for the tarnish-resisting chromium coating. Of the sixty-five samples sent in, sixty bore an outer coating of chromium, as against five carrying a surface coating of nickel. The majority of the parts were bright-chromium-plated : a few parts only, e.g. door handles, running-board rails, had a matt finish.

Nickel plays an increasingly important rôle as an underlay to chromium, and the data contained in the present report amply demonstrate the desirability of thick nickel coatings as a means of enhancing the corrosion-resistance and other properties of the superimposed chromium coating.

The chromium coatings on the ferrous, brass and bronze specimens were free from macroscopic defects, and but few microscopically fine cracks were found. The zinc- and aluminium-base samples in some cases showed cracks in the coating. The experimental coatings, prepared under more strictly controlled conditions, did not differ

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[1] The literature relating to the individual aspects of the subject is referred to in the appropriate chapters.

materially in surface condition from the automobile parts produced
in run-of-work.

Thickness and Regularity of Plating. It is essential that metal
coatings should be of a certain minimum thickness, since adequate
protection of the basis metal, and the mechanical and other pro-
perties required in the coating itself cannot be attained with less than
a certain thickness of plating. Uniformity of thickness is also vitally
important ; methods for determining this property are discussed in
detail in Chapter II. In the investigation reported here the metallo-
graphic method was used, employing high magnification.

On the few components on which nickel was used as the exterior
coating the thickness of plating ranged from 2 to 8 μ. On the chromium-
plated components the thickness of the chromium was less than 1 μ,
with the exception of the bronze parts plated without underlay, and
one specimen of running-board rail, which carried deposits of 1·5
to 3·5 μ.

Fig. 194 (frequency of occur-
rence of all thicknesses less than
1 μ) shows that, irrespective of the
nature and thickness of the inter-
mediate layers, a large majority
of the components carried a
chromium coating of about 0·5 μ.
With few exceptions, the experi-
mental samples were also plated
with a 0·5 μ coating of chromium.

FIG. 194.—Frequency of Occurrence
of Various Thicknesses of Chromium
Coating on Automobile Samples.

The technique of chromium-
plating is not yet sufficiently far
advanced to ensure completely
uniform thickness in the coatings. In the automobile parts, varia-
tions on plane or slightly curved surfaces amounted to 20 per cent.,
and at corners, recesses or edges, the variation was frequently as high
as 100 per cent. Variations up to 20 per cent. were found on the
experimental samples.

Composite Types of Plating. Chromium is rarely deposited
without an underlay of another metal. The nature, number and thick-
ness of the intermediate layers vary very widely.

For iron and steel the most widely used combination appears to be
copper-nickel-chromium : the copper layer in most cases is only 0·4–
0·5 μ thick, while the nickel layer varies within very much wider limits.

On brass, the nickel-chromium combination is by far the most
usual ; the thicknesses of the nickel underlay again varies very widely,
viz. 2·5–25 μ. The nickel-chromium combination is usually preferred
also for bronze parts. Only a few firms submitted directly-chromium-

plated bronze components; these samples carried a thicker chromium coating (1·5–3·5 μ).

Various combinations are used on zinc-base parts, e.g. copper-nickel-chromium, brass-nickel-chromium, nickel-chromium. On the samples examined the thickness of the nickel varied from 1·8 to 4 μ.

In the case of aluminium alloy castings the combination nickel-chromium (nickel 3–4 μ) predominated.

In view of the above indication of an almost universal preference for a nickel underlay, the majority of the experimental samples were also plated with the nickel-chromium type of coating; the nickel underlay ranged from 5 to 25 μ, with a chromium coating of 0·5 μ.

Adhesion and Capacity for Deformation. Metal coatings should be capable of adhering to the basis metal under the various forms of stress and corrosion encountered in service, i.e. when exposed to mechanical and thermal stresses and to chemical attack. They must also be tough, ductile and capable of plastic deformation, in order to withstand mechanical stress without cracking.

Two types of test have been evolved for determination of adhesion, viz.:

1. Tests which measure the force required for separation of the coating from the basis metal by tearing or other mechanical method of removal.

2. Tests which determine the degree of deformation at which separation of the coating from the basis metal takes place.

Neither type of test gives an entirely accurate and reliable quantitative measurement of adhesion. Tests of the first type are complicated by mechanical difficulties, while those of the second type are affected by the capacity for deformation inherent in both the coating and the basis materials. Both forms of test are therefore limited to the determination of adhesion of the coating under a given form and degree of deformation.

After an investigation of the various methods of testing adhesion (close-bend, tensile, reverse-bend, cupping, ball-indentation), the close-bend method was selected for testing specimens of thin sheet form and the ball-indentation method for use on castings and thicker sheet samples.

Close-bend Tests. The coatings on the automobile parts showed, in general, good capacity for deformation and satisfactory adhesion. All the sheet specimens 0·5 to 1·8 mm. thick could be bent round a mandrel of 10 mm. (0·4 inch) diameter without cracking of the coating or separation of the coating from the basis metal. Further flattening of the arms of the test pieces caused cracking at diameters varying, according to the thickness of the specimen, from 0·75 to 4·25 mm. (0·03 to 0·167 inch). In some of the specimens scaling and peeling also occurred under these conditions.

In most cases the experimental coatings exhibited a greater capacity for deformation than the coatings on the automobile parts.

The observations made did not indicate that the thickness of the nickel underlay exercised any appreciable influence on the behaviour of the coatings in this respect. In general, heavy chromium deposits showed a lower capacity for deformation than thinner coatings.

Ball-Indentation Tests. All the automobile samples showed fine cracks at the position of the ball impression ; in some cases these occurred at the centre of the impression only, in others at both the centre and at the edge. Heavy chromium plating deposited without underlay showed coarser and more extensive cracking than thinner plating ; flaking and incipient peeling were observed only in the case of coatings on zinc-base die castings. In the majority of cases, however, zinc-base parts chromium-plated over heavy underlays of nickel remained free from cracks, indicating that a thick underlay of nickel increases the capacity of the chromium coating for plastic deformation.

Coatings which adhered well to the basis metal in some cases showed very poor results in the ball-indentation test ; conversely, some of the coatings which showed poor adhesion exhibited no specially characteristic defect when tested by the ball-indentation method. The indentation test is therefore primarily a means of determining the capacity of the coating for deformation and the results obtained by it cannot be used as a general gauge of adhesive quality.

Hardness and Wear-Resistance. Hardness and wear-resistance is required in metal coatings in order to provide adequate resistance to pressure and frictional effects occurring in service and maintenance.

Due to the extreme thinness of metal coatings, only the scratchhardness test is practicable and this method yields satisfactory results only if the loading of the diamond point is so low that the scratch does not puncture the plating. (For further discussion of this aspect of the question see p. 78.)

Chromium plating possesses twice or three times the scratch-hardness of nickel plating, but the hardness of individual specimens of chromium plating varies over a wider range than that of nickel plating. No consistent relationship could be established between scratch-hardness and the thickness of the chromium deposit or the nature or thickness of the underlay(s).

Wear-resistance was determined by means of a grinding process, in which the metal surface was ground under a fixed load against a felt disc, using chromic oxide abrasive. The loss in weight of the coating during 5 minutes' grinding, or the time required to grind through the chromium plating, was taken as the measure of wear-resistance.

Consistent with the results of the scratch-hardness tests, the wearresistance of chromium plating was found to be two to three times that

of nickel plating. In the case of the experimental samples, thick deposits showed markedly higher wear values than thinner platings. It was not found possible to establish any relation between the nature and thickness of the interlays and the wear-resistance.

Behaviour under High-Temperature Conditions and Conditions of Alternating Temperature. Metal coatings should be capable of withstanding raised temperature conditions without tarnishing and able to sustain the temperature variations met with in service without cracking or other impairment of physical or mechanical properties.

Tarnish-Resistance. For the purpose of determining the conditions producing incipient tarnishing (oxidation), observations were made on changes in surface condition of specimens after heating for stated periods at fixed temperatures.

Incipient pale yellow tarnish colours were observed on nickel plating after heating for 5 hours at 330° C. : chromium plating was completely unchanged after heating for 5 hours at 400° C. Commencement of tarnishing in chromium plating occurs at temperatures about 150° C. higher than those required to produce a similar effect on nickel plating. In view of the fact that the initial reflectivity of the two metals is approximately equal and that chromium retains its lustre longer than nickel under exposure to high temperatures, chromium is the more suitable form of coating for reflectors.

Resistance to Alternations of Temperature. Behaviour under reversals of temperature was tested by repeated heatings to 300° C. and quenching in water at room temperature, the cycle being repeated until cracking or peeling of the coating set in.

The behaviour of metal coatings under alternations of temperature is influenced to an important degree by the differences in the coefficient of thermal expansion existing between the metals which are in contact with one another. If the differences are very great, stresses of considerable magnitude are set up between the deposit and the basis metal and ultimately lead to cracking and flaking of the coating. Since the coefficient of thermal expansion of chromium is considerably lower than that of any of the metals or alloys generally used in immediate contact with it, chromium plating deposited directly on the basis metal tends to crack under alternating temperature conditions. Thick deposits show the defect in a greater degree than thinner coatings. If, however, a layer of a metal of intermediate coefficient is placed between the basis metal and the chromium coating, the stresses arising on change of temperature are markedly reduced and the danger of cracking is lessened. Nickel has proved to be pre-eminently suitable for use as an underlay for chromium.

Porosity. A coating metal which is more noble in the electro-

chemical series than the basis metal on which it is plated can protect the latter from corrosive attack only so long as the coating is dense and free from porosity. Since chromium and nickel are more noble than the metals used as foundation materials, maximum freedom from porosity in the coatings is a primary essential.

Both chemical and electrochemical methods may be used for determining porosity. The chemical processes are based on the reactions of indicator solutions with the ions of the basis (or underlay) metals passing into solution at the pores of the outer coating. For testing chromium plating on iron-, brass- or bronze-base articles, the ferroxyl indicator is suitable ; for chromium coatings on a nickel underlay, dimethylgyoxime is the preferred indicator. Coatings on aluminium or zinc alloys may be tested by means of sodium hydroxide solutions which act by producing hydrogen bubbles at the porous spots on the coating. The electrochemical method employs an acid copper sulphate solution, in which the specimens are immersed or exposed to mild cathodic treatment : copper is precipitated at the pores on the coating.

The investigation has shown that chromium plating absolutely free from porosity is rarely produced, but that the number of pores penetrating to the basis metal may be greatly reduced by regulation of the nature and thickness of the intermediate layers used under the chromium.[1] For example, samples chromium-plated over a thick three-fold underlay, viz. nickel 7, copper 6, nickel 33 μ, or nickel 7, copper 35, nickel 2 μ, showed much lower porosity than any other samples examined (ratings 0·03 and 0·06 respectively). The ratings of the other chromium-plated automobile parts varied widely, but in all cases the decrease in porosity produced by increasing thickness of nickel underlay was clearly evident, the effect being even more pronounced in the experimental than in the automobile samples. An underlay of nickel is also advantageous from other points of view (e.g. under alternations of temperature : *vide supra*).

Corrosion-Resistance. Since chromium itself is practically immune from attack by water, salt solutions and other substances with which plated parts come in contact, any deterioration which may occur must proceed from the basis or underlay metal(s) through the pores of the chromium coating. Corrosion tests for use on chromium-plated parts must, therefore, be of a somewhat specialised type. The method adopted in the present investigation was the determination of the length of time required to cause permanent damage to the coating (incipient scaling or peeling) by the respective corrosive agents. The results of

[1] The nickel layer should not be less than 15 in. thick, and the corrosion-resisting properties of the coatings are appreciably enhanced by increasing the thickness to 25 μ.

these experiments, both on the automobile parts and the experimental samples, gave definite proof that the behaviour of the chromium coating is influenced to an important degree by the number of pores penetrating through to the basis metal.

The number of pores decreases with increase in thickness of the interlay deposits, and the life of chromium coating, in so far as it is dependent on resistance to corrosion, will therefore be primarily a function of the nature and thickness of the intermediate layer(s). This conclusion is confirmed by all the tests made in the present investigation. A thick intermediate layer of nickel is especially effective in securing increased resistance to corrosion and resulting increase in life of the chromium plating.

Basis Metals. Two factors influence the choice of basis material : first, the mechanical properties required in the component, and, second, the corrosive and other effects which will be encountered in service. Where strength and elasticity are primary essentials, iron, steel or brass will be used, brass being preferred for parts likely to be frequently exposed to moisture, e.g. for exterior automobile parts. Iron or steel, on the other hand, is preferred to brass for components exposed to frequent variations of temperature, e.g. lamp reflectors. For castings in which high mechanical strength is required, bronze has many advantages, while if high strength is not essential, aluminium- or zinc-base castings may be employed. In view of their lower resistance to corrosion, however, aluminium- or zinc-base castings are preferably used for interior parts only.

Greasing of Plated Parts. Greasing of chromium-plated parts when out of use is strongly recommended. The grease in the pores of the chromium coating will confer protection on the more corrodible basis metal for a considerable length of time.

<center>ADDENDUM</center>

For purposes of comparison, a summary is given below of the conclusions drawn by the Joint Committee of the American Electroplaters' Society, the American Society for Testing Materials and the National Bureau of Standards in their exposure and accelerated tests of nickel and chromium coatings on ferrous materials [485 and 537] :

Atmospheric Exposure Tests

"1. The protective value of nickel coatings depends almost entirely on their thickness. At least 0·0005 inch (0·013 mm.) is required for good protection under mild conditions, and at least 0·001 inch (0·025 mm.) for severe conditions.

2. Within the range of controlled conditions under which the experimental coatings were produced, the conditions of nickel

deposition and of the cleaning and pickling have no marked effects on the protective value.

3. The presence of a layer of copper reduces the protective value of thin nickel deposits under all conditions, and of thick deposits under severe conditions. If chromium is also present, the copper has very little harmful effect in thick deposits. If the copper layer is buffed, the protective value of the composite coating is increased.

4. A very thin deposit of chromium, such as 0·00001 inch (0·00025 mm.) sometimes reduces the protective value, especially of pure nickel deposits. Chromium coatings about 0·00002 to 0·00003 inch (0·0005 to 0·0008 mm.) add very little to the protective value, but maintain their bright appearance owing to their resistance to tarnish. Relatively thick chromium coatings, from 0·00005 to 0·0001 inch (0·0013 to 0·0025 mm.) improve the protection against corrosion, especially in an industrial atmosphere.

5. The protective value of chromium over nickel or composite coatings is somewhat improved by using a bath with a high ratio, $\dfrac{\text{g./l. CrO}_3}{\text{g./l. SO}_4}$ such as 200. Deposits produced at 35° C. (95° F.) are slightly superior to those made at somewhat higher temperatures.

6. The use of zinc under nickel makes the protective value less than that of either metal alone. Cadmium has very little effect under nickel [cf. 528, 529].

7. The use of zinc or cadmium under nickel tends to produce white stains and blisters.

It is noted that conclusions drawn by Jacquet [398] from exposure tests made on the roof of a building in Paris are largely consistent with the results of the tests made by the American Joint Committee."

Accelerated Tests

" Both the exposure tests and the accelerated tests showed clearly that the protective value on steel of coatings consisting of the more noble metals, such as copper, nickel or chromium, depends almost entirely on their freedom from porosity. If it were possible to produce absolutely impervious coatings of this group, especially of chromium, they would furnish permanent protection in most climates. Reliable tests for porosity may therefore be very useful for inspection, as they require much less time than the usual accelerated corrosion tests.

" Both the salt-spray and intermittent immersion tests are useful for determining the relative quality, and especially the porosity of coatings consisting of copper, nickel and chromium. The results are more significant and more closely related to those of

atmospheric exposure if the number and size of the rust spots at the end of a specific period, such as 100 hours, are recorded, rather than the time for the first appearance of rust. These methods do not, however, closely reproduce the types of corrosion produced in the atmosphere, and do not serve to detect small differences in protective value. The ferroxyl test is a rapid, reliable method of determining the relative porosity of coatings."

Recommendations are made with reference to optimum conditions for the ferroxyl test (see p. 10, Chapter I).

See also specifications based on these conclusions, p. 41.

APPENDIX

CONVERSION TABLE (μ, mm., in.)

μ	mm.	in.
0·1	0·0001	0·000004
0·2	0·0002	0·000008
0·3	0·0003	0·000012
0·4	0·0004	0·000016
0·5	0·0005	0·00002
1·0	0·001	0·00004
5·0	0·005	0·0002
10·0	0·01	0·0004
15·0	0·015	0·0006
20·0	0·02	0·0008
25·0	0·025	0·001
30·0	0·03	0·0012
35·0	0·035	0·0014
40·0	0·04	0·0016
45·0	0·045	0·0018
50·0	0·05	0·002
100·0	0·1	0·004
110·0	0·11	0·0044
120·0	0·12	0·0048
130·0	0·13	0·0052
140·0	0·14	0·0056
150·0	0·15	0·006

Throughout the report, conversions to English units of measurement are approximate.

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    † denotes text-book literature.

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AUTHOR INDEX

Note.—Item numbers of the bibliography are in bold face : numbers of the pages where the reference is quoted follow the bold-face numerals.

S

SUBJECT INDEX

259